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(ZHURNAL ANALITICHESKOI KHIMII)

IN ENGLISH TRANSLATION

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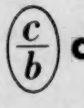

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ANALYTICAL CHEMISTRY AND THE TWENTY-SECOND CONGRESS OF THE COMMUNIST PARTY OF THE SOVIET UNION

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 657-659, November-December, 1961

The twenty-second Congress of the Communist Party of the Soviet Union will sum up socialist construction in our country and will indicate the path to be taken for constructing a communist society.

In connection with the wide development of a communist structure important new problems confront analytical chemistry just as they confront other sciences.

Of no little importance in the development of analytical chemistry in the Soviet Union has been the successful development of the theoretical bases of analytical methods, and the development of the theory of the analytical chemistry of individual elements in Mendeleev's Periodic Table. A considerable amount of work has been carried out in developing rapid and accurate methods of qualitative and quantitative determination of any amounts of elements and compounds independently of the presence of other elements. Important results have been achieved in the search for new possibilities of controlling chemical reactions underlying analytical methods. Research work along these lines has been concentrated on studying chemical equilibria, on the effect of varying conditions on the path of chemical reactions and the stability of the simple and complex compounds formed, on studies of redox potentials, formation of compounds insoluble in a given medium, and colloid formation, and on the study of the structure of indicators and the nature of the color of compounds. One must point out the successful development in our laboratories of the theory and practice of the use of organic reagents in analysis, the development of extraction methods and ion exchange, and also the study of coprecipitation mechanisms. The wide use of the latest achievements in molecular physics, electron optics, radiochemistry, and sorption techniques, play an important role in developing all these problems.

In recent years systematic studies have been successfully carried out on chemical reactions of individual elements, mainly of the rare and scattered elements by modern physicochemical methods from the point of view of the demands placed on them by analytical chemistry. This has made it possible to change over from developing individual analytical methods, from solving special problems in the analytical chemistry of an element to developing a theory for the analytical chemistry of an element, to generalization of factual material, i.e., to creating a scientific basis for current and newly developed analytical methods. The chemical similarity and differences between elements in different valence states are being studied more thoroughly on the basis of the periodic law.

One must emphasize the need for further development of material (phase) analysis and of systematic organic analysis on the basis of the latest achievements in the field of the determination of functional groups. Inorganic phase analysis and organic analysis are still one of the least developed branches of analytical chemistry. At the same time phase analysis is of great importance for mineralogy, metallurgy, metal treatment, the silicate industry, and the technology of certain industries, for which ordinary chemical analysis is not adequate, while information on the real forms of compounds in natural and technical materials is needed.

Analytical chemistry is of exceptional importance for the various natural sciences and for the control of modern production. At present analytical methods play a particularly important role in the study of the conversion of certain materials into others. Such analytical methods as radioactivation analysis, mass-spectroscopy, spectographic analysis, and spectrophotometry, have played an important part in organizing and improving the production of pure and superpure materials in modern metallury, for which the use of the so-called rare and scattered elements is a characteristic feature. Analytical methods have acquired great importance in the study and development of natural sources of raw material. The geological service has at its disposal at present a well developed chain of splendidly equipped laboratories of different types. Production control is of great importance in the chemical, atomic, power, petroleum, pharmaceutical, food and other branches of industry. Analytical chemical control has played an exceptionally important part in improving many industries.

Analytical chemical control and analytical chemical methods are developing with increased tempo in conjunction with the creation of more highly efficient and economically profitable methods of high tonnage organic synthesis—development of natural and byproduct gases, coal, petroleum, various plant wastes—which makes it possible to

obtain starting materials for the synthesis of polymeric and other materials. Nevertheless, the analysis of organic materials is characterized by the methods required and has still not been developed sufficiently to be separated from organic chemistry.

The expansion of research in the fields of the rare elements and semiconducting materials, the preparation of plastic and other high molecular weight materials, the solution of problems relating to the production of synthetic materials with given properties have demanded that analytical chemists develop theory further and develop new analytical methods.

Analytical chemistry has played its part in agricultural chemistry—including such important natural reserves as soil (microelements, fertilizer analysis, etc) plant and animal materials—and also in the study of metabolism in the organism without destroying the totality of the functioning living tissue and without halting the living processes and interfering in their function. The production of antibiotics, vitamins, and other physiologically active materials would be impossible without a well established analytical chemical control.

The large volume of production control and the short time within which it has to be carried out have compelled analysts to search for new ways of speeding up work in analytical laboratories. With the ever increasing number of elements for which production control is necessary, demands for increasing accuracy and tempo can only be satisfied by developing selective reactions and methods, which can be carried out without removing the elements which normally interfere, and which enable systematic classical analysis to be avoided.

One must note the undoubted successes achieved in ensuring maximum automation of actual analytical methods based on spectrographic analysis, spectrophotometry, electrochemical methods, and the use of radioactive indicators. This in turn has opened up the way to automatic analytical chemical control of production processes.

Solution of new problems would be impossible without essentially improving the training of cadres of analytical chemists and increasing their number. The respective departments in the universities have carried out a lot of work along these lines.

Such important branches of industry as the metallurgical, atomic, aviation, and petroleum industries have at their disposal modern, well equipped laboratories. Production of pure and specially pure reagents in the required amounts has been organized.

A large amount of scientific and scientific-technical literature is published in our country on analytical chemistry. Among them one must point out the series of monographs on the analytical chemistry of the most important elements, the textbooks on the analysis of pure materials and on the analytical chemical control of production.

Analytical chemistry is developing very rapidly in the USSR and strongly influences the progress of other natural sciences and technical production. In the last ten years an outstanding analytical school has arisen which is developing new progressive theories and is giving many valuable practical results.

Soviet scientists inspired by the Communist Party, shoulder to shoulder with all the workers in our country raise the bright edifice of communism. Together with the whole nation they subjugate and overwhelm nature, use its powerful forces in the interest of peace and progress, and create huge material and spiritual values. There is no doubt that the ranks of scientists will grow and strengthen, supplemented by new cadres, who will make our country famous and enrich its advanced science with new, outstanding achievements and discoveries.

THE EFFECT OF THE DEGREE TO WHICH TEST MATERIAL IS GROUND ON THE RESULTS OF QUANTITATIVE SPECTROGRAPHIC ANALYSIS BY THE BLAST METHOD

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The possibilities of the air blast method [1-5] which we have successfully used for three years in a somewhat modified form for quantitative analysis have been confirmed by daily practice. Several hundred analyses have been carried out, in the main only in the State Institute of Applied Chemistry (SIAC). Several institutes and plants have adopted the general features of the SIAC method [2]. In this connection the article by Raikhbaum and Luzhinova[3] has evoked considerable interest. The authors of this article established that there is a strong relationship between line intensity and the extent to which the test material has been ground when the spectra are excited by the spraying–blast technique of Rusanov in an AVR-2 apparatus [5]. This fact testifies to incomplete evaporation of particles in the arc discharge. When the particles have been ground very finely they coagulate again, and the effect does not disappear [3]. Since accurate reproducibility and control of the granular composition of the test material are impossible under analytical conditions, it follows from [3] that it is doubtful whether or not the blast method can be used successfully for quantitative analysis.

The characteristic feature of the blast method used in SIAC is the introduction of the powdered material into the arc by means of an air stream [2]. We have examined the relationship between line intensity and the extent to which the powder has been ground. For this purpose test materials of the slag type were sintered with oxidizing agents [4] and the product obtained ground and then sieved. Two types of powders were prepared which differed from each other in the way in which the internal standard was introduced. In one case the internal standard (cobalt) was introduced before sintering, and, consequently, before grinding, while in the second case the internal standard was introduced after the test material had been finally ground. The ground samples were diluted five times with carbon powder sieved through a No. 32 sieve.

The spectra were photographed in a medium type spectrograph at a current of 15 amps under standard conditions [2]. Lines used in slag analysis were measured photometrically. The relationship between line blackening and the value of ΔS on the degree of grinding are given in the tables.

Initially, experiments were carried out with powders ground in a mortar and sieved through various sieves. Cobalt in the form of aliquots of Co_2O_3 was introduced separately after grinding to each fraction. The results are given in Table 1.

In order to give an idea of the reproducibility of ΔS values, when photographs were taken in parallel, the table, in addition to containing abridged results for various elements, contains detailed factual material on manganese. It follows from the table that the line intensity of all elements increases with decreasing size of particles passing into the arc discharge. In this connection there occurs a sharp increase in the value of ΔS. Since we did not have very fine sieves it was not possible in the course of this experiment to follow changes in line intensity, when the test material was ground even finer. Accordingly, we carried out an additional experiment, results of which are given in Table 2. In this case, the material, after sintering, was divided into seven parts and each part ground in an IS apparatus for 1.5 to 20 min. Cobalt was introduced after grinding.

It follows from Table 2 that test material is ground to a very fine state in the IS apparatus in 2.5-3 min, while the intensity to a very fine state in the IS apparatus in 2.5-3 min, while the intensity and also the ΔS values hardly change at all even when the test material is treated for a considerably longer time. The small increase in the line intensity of silicon can probably be attributed to contamination of the test material by a plastic material from which

the boat in which the material to be ground is placed. The experiments described convincingly demonstrate that the analytical results obtained when the blast method is used will not depend on the degree to which test material has been ground, as long as the fineness of grinding exceeds a certain value which can be achieved in practice in an IS apparatus.

TABLE 1

Sieve size, mm	S Mn	S Co	ΔS Mn	ΔS_{mean} Mn	S Fe	ΔS_{mean} Fe	S Al	ΔS_{mean} Al	S Si	ΔS_{mean} Si	S Ca	ΔS_{mean} Ca
0,125	52 55 41	116 125 105	—064 —0,70 —0.64	—0,66	29 32 21	—0,84	62 69 51	—1,10	38 48 28	—1,33 —	 —	
0,100	60 67 67	95 104 108	—0,35 —0,37 —0,41	—0,38	33 34 36	—0,68	90 94 94	—0,75	50 55 53	—1,15	20 23 24	—1,46
0,074	113 115 118	111 115 117	0,02 0,00 0,01	0,01	65 67 77	—0,43	145 150 153	—0,34	85 91 90	—0,95	64 65 68	—1,18
0,063	131 123 122	113 — 107	0,18 — 0,15	0,16	87 86 84	—0,25	167 167 170	—0,14	101 100 96	—0,83	81 79 81	—1,01
0,056	149 147 150	104 100 106	0,43 0,47 0,44	0,45	98 101 101	—0,01	193 191 195	0,21	106 106 110	—0,65	100 99 99	—0,73
0,044	168 165 162	111 110 107	0,57 0,55 0,55	0,56	124 125 122	0,15	210 210 210	0,34	129 122	—0,51	113 108 107	—0,67

TABLE 2

Grinding time, min	S Fe	S Co	ΔS Fe	ΔS_{mean} Fe	S Mn	ΔS_{mean} Mn	S Al	ΔS_{mean} Al	S Si	ΔS_{mean} Si	S Ca	ΔS_{mean} Ca
1,5	53 47 52	110 98 114	—0,57 —0,51 —0,6	—0,57	83 75 83	—0,27	86 82 87	0,48	66 64 73	—0,59	38 36 39	—0,95
2	112 111 108	107 107 103	0,05 0,04 0,03	0,05	152 155 153	0,48	151 156 152	1,23	107 112 108	—0,23	95 93 92	—0,38
2,5	98 106	97 107	0,01 —0,01	0,01	142 152	0,45	147 156	1,34	102 109	—0,27	92 100	—0,37
6	98 101	101 106	—0,03 —0,05	—0,04	143 148	0,42	154 158	1,31	113 117	—0,17	90 90	—0,42
8	98 97 102	99 93 99	—0,01 0,04 0,03	0,02	142 136 142	0,42	150 149 154	1,30	110 115 116	—0,16	87 82 88	—0,44
13	93 98 97	104 109 111	—0,11 —0,11 —0,14	—0,12	140 147 147	0,37	153 158 158	1,25	116 122 120	—0,13	88 90 91	—0,43
20	97 100 107	103 106 113	—0,06 —0,06 —0,06	—0,06	141 144 151	0,38	156 160 166	1,31	118 121 122	—0,15	83 88 —	—0,48

It was of interest to follow the change in ΔS values in those cases where the internal standard was introduced before sintering, and accordingly, was subjected to grinding at the same time as the bulk of the test material. Table 3 contains the results of such an experiment. Each of samples 1-6 is a powder which passed through a given

sieve but was retained on the next, finer sieve. These samples were prepared by grinding the powder in a mortar. Samples 7-9 were prepared by grinding fraction 6 in an IS apparatus for 4, 7, and 10 min, respectively.

TABLE 3

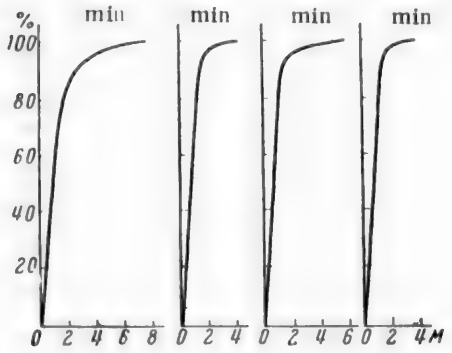
Sample no.	Sieve size, mm	S Mn	ΔS_{mean} Mn	S Fe	ΔS_{mean} Fe	S	ΔS_{mean} Al	S Si	ΔS_{mean} Si	S Ca	ΔS_{mean} Ca
1	0,12	16 12	—0,12	10 7	—0,18	37 31	—0,45	13 13	—0,67	— —	—
2	0,125	51 52	—0,25	25 27	—0,50	85 91	—0,59	39 42	—1,07	21 21	—1,26
3	0,100	71 72	—0,29	36 38	—0,66	94 93	—0,59	51 50	—1,02	35 35	—1,17
4	0,083	97 103	—0,30	51 56	—0,76	101 102	—0,62	59 64	—1,06	53 59	—1,07
5	0,056	118 129 127	—0,29	75 84 83	—0,73	90 101 97	—0,62	61 72 66	—0,92	74 80 80	—0,85
6	0,044	122 114 115	—0,30	83 76 76	—0,69	94 79 85	—0,60	65 53 53	—0,89	75 69 71	—0,74
7	—	102 97 82	—0,33	71 66 56	—0,64	95 98 102	—0,49	58 55 53	—0,92	57 58 45	—0,94
8	—	90 88 85	—0,32	50 48 46	—0,72	90 97 98	—0,47	51 53 53	—0,89	49 50 48	—0,93
9	—	85 91 97	—0,30	44 47 53	—0,73	94 99 101	—0,45	49 55 57	—0,89	48 50 54	—0,92

It is clear from Table 3 that it is also possible, when an analysis is carried out, to introduce the internal standard before sintering, since after treatment of the test material in an IS apparatus, the ΔS values for all the elements tested becomes independent of the grinding time. For analytical purposes, it is more correct to introduce the internal standard before sintering, since cobalt should be distributed more evenly in the test material when this technique is employed, while the ΔS values will be independent of the degree of grinding over wider limits.

Thus, all the experiments carried out show that after the particles have been ground to a certain fineness, the line intensity of Mn, Fe, Si, Al, Ca, and Co, within the limits of experimental error, remains constant and is independent of a further increase in grinding time. An attempt was made to estimate the degree of grinding of test material by measuring the particle size on a MIP-4 polarizing microscope at a magnification of × 720. Shapeless aggregates of very weakly aggregated particles as well as individual particles were visible in the field of vision of the microscope. At lower magnifications it is readily seen that when the aggregates are touched slightly adhesion of the particles is destroyed. Powders ground in the IS apparatus for 1.5, 3.5, 8, and 13 min were examined under the microscope. Results of measuring a large number of individual particles are presented in the diagram. It follows from these curves that approximately half the particles have a diameter of down to 1 μ, while 90%, of all the particles have a diameter between 1.5 and 2 μ. The granular state of the powders was very homogeneous, as long as one does not take into account the powder obtained on grinding for 1.5 min. Apparently, grinding for more than 3 min only increases the fineness very little, while the line intensity hardly increases at all after 2-3 min grinding.

It can be assumed that the very unstable, friable accumulations of particles observable under the microscope are destroyed just by mixing the ground powder with carbon powder. The latter is not ground in the IS apparatus but is prepared by grinding carbon electrodes with a cutter and then sieving the powder through a coarse No. 32 sieve.

During vigorous mixing with the ground sample in a mixer, these coarse particles of carbon powder should affect the material being ground and break down the aggregates of particles of the sample. The air blast should have the same effect. Accordingly, the fraction of aggregated particles in the total mass of the powder, is presumably, insignificant, and the evaporation of the test material is determined by the individual particles. Whether or not particles of diameter up to 2 μ evaporate completely during their passage through the arc flame is a question which can only be solved from indirect signs. Should the fraction of aggregated particles be high, while the aggregates and individual particles only succeeded in partially evaporating, the line intensity and ΔS values would vary so strongly, that quantitative analysis would be impossible; this is not observed in practice. Accordingly, we suggest that complete evaporation of the overwhelming majority of the particle occurs in an arc discharge.



The relation between the granular state of powders and grinding time in the IS apparatus.

One can conclude that the results of analyzing materials of constant composition by the blast method are independent of the degree to which the samples and standards have been ground, as long as a certain degree of fineness readily achieved in practice is ensured.

SUMMARY

When spectra are excited by the blast method, line intensity is dependent on the degree to which test material has been ground. When the material is very fine (when not less than 90% of all the particles have a diameter not exceeding 2 μ) particle size no longer affects the analytical results. An instrument is recommended which ensures that powders are ground to the requisite fineness in 2-4 min.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE MUTUAL INFLUENCE OF THE ALKALI METALS DURING THEIR DETERMINATION BY FLAME PHOTOMETRY

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Other elements which are present in the flame affect the radiation intensity of a test element. In the case of the alkali metals this effect is most strongly shown in the case of the radiation intensity of Cs, Rb, and also K; the effect is much weaker for Na and is almost completely absent in the case of Li.

It is desirable to establish what is the order of the change in intensity one can expect in each separate instance, and also to establish the reasons for such changes. There is an appreciable amount of published material on this question; this refers mainly to changes in the radiation intensity of sodium, potassium, and lithium [1-29]. The work described here is also devoted to a study of the mutual effect of alkali metals when working with a flame. A series of experimental results is given, while an attempt is also made to calculate the magnitude of this effect on the basis of theoretical premises.

The work was carried out with an air-acetylene flame using an atomizer and a burner of the Zeiss type. A FÉU-22 photomultiplier was fitted directly onto the outlet slit of an UM-2 monocrhomator and a voltage of 1100 -1200 v was applied to the photomultiplier from a high voltage stabilized rectifier. The current which developed was measured with a mirror galvanometer having a sensitivity of 10^{-9} amp/mm. The flame was arranged at a distance of 10-12 cm from the monocrhomator slit at such a height that the blue cone of the flame was 10-12 mm lower than the slit; the width of the inlet and outlet slits was 0.10 mm. The following lines were used for measurement: for Li, 670.8 mμ; Na, 589.3 mμ; Rb, 780.0 mμ; Cs, 852.1 mμ. The following experiments were carried out.

1. A study was made of the change in radiation intensity of lithium, sodium, rubidium, and cesium at a concentration of 10 mg/liter on adding 5000 mg/liter of KCl to each of the solutions. The ratio I/I_0 was taken as a measure of the effect of this mutual influence, where I is the intensity of the radiation of the test element when KCl has been added, and I_0 the intensity in the absence of potassium, as was done during a study of the effect with a dc arc [30]. For similar experimental conditions the ratio I/I_0 is a reasonably constant value.

It follows from Table 1 that the effect is greater the higher the atomic weight of the test element, the difference being very great: there is a hardly observable change in the intensity of the lithium line at 670.8 mμ on adding KCl; the intensity of the cesium line (852.1 mμ) on the other hand increases 27 times.

TABLE 1. Effect of 5000 mg KCl/liter on the Radiation Intensity of Li (670.8 mμ); and Rb (780.0 mμ), and Cs (852.1 mμ); taken from experimental results

0 mg/liter of the element taken	Ratio of intensities I/I_0
Li	0.99
Na	1.2
Rb	9.1
Cs	26.9

TABLE 2. Effect of 5000 mg KCl/liter on the Radiation Intensity of Rb (780.0 mμ), Introduced into the Flame in the Form of RbCl, $RbNO_3$, and Rb_2SO_4

10 mg Rb/l taken in the form of	Effect of KCl at a concentration of 5000 mg/liter
RbCl	9.10
$RbNO_3$	9.04
Rb_2SO_4	8.99

2. In subsequent experiments we established the effect of various concentrations of KCl and NaCl (50, 500, and 5000 mg/liter) on the radiation intensity of rubidium at a concentration of 10 mg/liter, and also studied the effect of the same KCl or NaCl content (5000 mg/liter) on the radiation intensity of Rb at various concentrations of the latter (10, 20, 30, 40 mg/liter). The results obtained are given in Figs. 1-4*. It is clear from the curves that on increasing the KCl and NaCl concentration from 50 to 5000 mg/liter, their effect on the intensity of the Rb line increases; the increase in intensity being greater on adding KCl than on adding NaCl. At low rubidium concentration, the calibration curve has a parabolic shape (similar calibration curves are also obtained at low Cs and K concentrations).

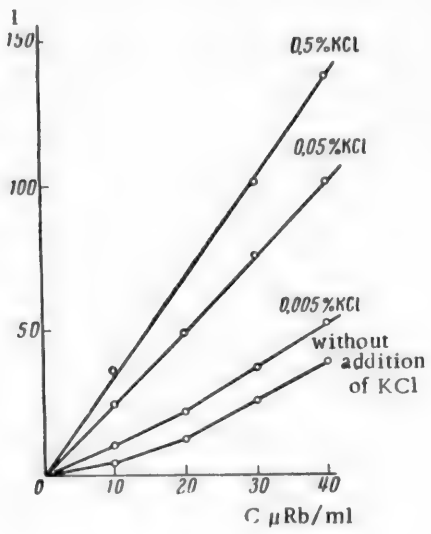

Fig. 1. Calibration curves for Rb (780.0 m μ) with and without addition of varying amounts of KCl.

As the concentration of the element added is increased the radiation intensity of Rb increases and the curve straightens out. At a KCl (or NaCl) concentration of 5000 mg/liter the curves are linear. In order to demonstrate more clearly the relation between the effect of 5000 mg/liter of KCl and NaCl on the

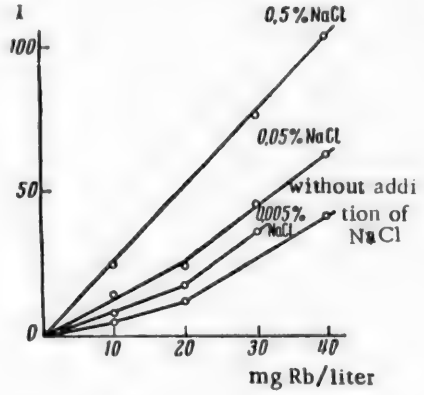

Fig. 2. Calibration curves for Rb (780.0 m μ) with and without addition of varying amounts of NaCl.

radiation intensity of rubidium and the concentration of the latter, curves are shown in Figs. 3 and 4 which are constructed within the coordinates $C-I/I_0$. These curves show that on increasing the Rb concentration from 10 to 40 mg/liter while the same amount of KCl or NaCl is added, the effect weakens.

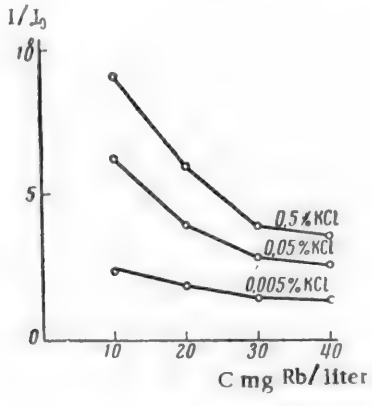

Fig. 3. Effect of equal amounts of KCl on the radiation intensity of various amounts of Rb (780.0 m μ).

3. KCl at a concentration of 5000 mg/liter was added to three solutions of rubidium introduced into the flame in the form of different compounds RbCl, $RbNO_3$, and Rb_2SO_4 at concentrations of 10 mg/liter—calculated as rubidium. The effect was the same for all three compounds (Table 2).

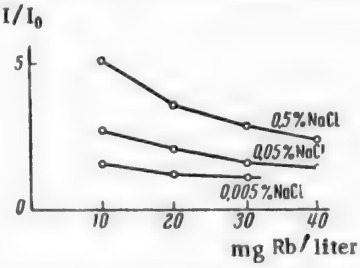

Fig. 4. Effect of equal amounts of NaCl on the radiation intensity of various amounts of Rb (780.0 m μ).

*When this work had been finished and had been sent for publication, the article by Fabrikova appeared [31]; this article contained calibration curves similar to those given in Figs. 1 and 2 for Rb concentration from 0 to 100 mg/liter without addition of potassium, and with addition of 500, 1000, and 2500 mg potassium/liter.

Discussion of Results. The reasons leading to changes in the radiation intensity of the test elements in the presence of other elements may be of three types [13,33].

1. Interference which arises from the radiation of the flame and from overlapping of the lines by the lines or bands of foreign elements, this effect is shown up by a deviation of the galvanometer when the apparatus is adjusted to the lines of the test element for solutions of other salts introduced into the flame. Such interference was taken into account in our experiments.

2. The second type of interference and effect arises as a result of changes in the spraying or evaporating conditions of the drops, and also as a result of changes in the flame temperature. Poluektov et al.[33] on the basis of experimental results obtained with two atomizers are of the opinion that when working with solutions of alkali metal salts, the added alkali metal does not change the properties of the solution which affect the atomizing process, but rather mainly affect processes occuring in the flame. In our case the amount of solution containing 10 mg Rb/liter passing each second into the flame, with and without addition of 5000 mg KCL/liter, was almost the same.

The flame temperature only changes on introducing large concentrations of the alkali metal salts. Thus Tskhai and Mandel'shtam [34] have shown that the flame temperature starts to change on adding sodium at concentrations higher than 1 M; in our case the concentrations of NaCl and KCl added did not exceed 0.1 M.

3. One must take into account the effect connected with changes in the degree of dissociation of the molecules and the degree of ionization of the atoms of the test element in the presence of foreign elements. At the temperature of an air-acetylene flame the degree of dissociation at low concentrations of the alkali metals (partial pressure of the atoms $n \times 10^{-8}$ atm) will change very little on adding other alkali metals*. On the other hand, it is the change in the degree of ionization of the test element on adding to its solution another alkali element whose atoms themselves ionize and increase the concentration of free electrons in the flame, which is the main reason for the change in radiation intensity of test elements [13, 36-41].

We have calculated the change in the radiation intensity of Li, Na, Rb, and Cs on adding KCl and NaCl to solutions of their salts, on the assumption that these changes are solely the result of changes in the degree of ionization of the atoms of the test elements. The results obtained are in reasonably good agreement with experiment.

Calculations were carried out on the basis of the following formulas [13, 38, 39, 40, 41]:

$$\frac{p_1^+ p_e}{p_1} = K_1 \ldots (1); \quad P_1 = p_1 + p_1^+ \ldots . \tag{2}$$

Since, in this case, when there are no foreign elements present in solution $p_1^+ = p_e$, equation (1) can be written in the following form [13]:

$$\frac{(p_1^+)^2}{p_1} = K_1 .$$

where p_1^+, p_1^- are the partial pressures of the ionized and neutral atoms of the test element; p_e is the partial pressure of the electrons; P_1 is the partial pressure of the total number of atoms of the test element, both ionized and unionized; K_1 is the ionization constant of the test element at a given temperature. The ionization constant was calculated by means of the formula:

$$\lg K = \frac{-5040\,U}{T} + 5/2 \lg T - 6{,}49, \tag{3}$$

where T is the flame temperature in °K; U is the ionization potential of the test element in ev.

According to [13, 37, 42, 44] the temperature of an air-acetylene flame is 2530-2360°K. We adopted a value of 2430°K after correcting it so that the effect for Rb at a concentration of the latter of 10 mg/liter on adding 5000

* Approximate calculations which we made on the basis of formulas taken from [3] for the degree of dissociation of Rb at a concentration of 10 mg/liter with and without addition of 5000 mg KCl/liter confirmed our assumptions. Formation of sparingly volatile and little dissociated compounds has only been observed for lithium, and not for the other alkali elements [11].

mg KCl/liter, was close to the experimental value when all the remaining data were in good agreement with experiment. At this temperature the ionization constants were as follows:

$$K_{Li} = 6{,}22 \cdot 10^{-10}$$

$$K_{Na} = 2{,}11 \cdot 10^{-9} \qquad K_{Rb} = 2{,}06 \cdot 10^{-7}$$

$$K_{K} = 9.4 \cdot 10^{-8} \qquad K_{Cs} = 7 \cdot 98 \cdot 10^{-7}$$

For evaluating P we assumed that the experimental conditions we used were similar to those in [42, 43, and 44], in which the total number of atoms in 1 cm^3 of the flame was considered to be given by

$$N_{total} = 6.2 \times 10^{14} \text{ c atoms/cm}^3 \tag{4}$$

where c is the concentration of the salt in solution, M; from which

$$P_1 = \frac{6{,}2 \cdot 10^{-14} c}{\frac{N_0}{V_0}\frac{273}{2430}} = 2 \cdot 10^{-4} c \text{ atm}, \tag{5}$$

where N_0 is the Avogadro number, V_0 is the volume occupied by a mole of an ideal gas. For cases in which potassium and sodium salts were introduced into the solution, three equations were solved [13, 41]:

(6)

$$\frac{p_1^+ \cdot p_e}{p_1} = K_1 \ldots \tag{7}$$

$$\frac{p_2^+ \cdot p_e}{p_2} = K_2 \ldots \tag{8}$$

$$p_e = p_1^+ + p_2^+$$

it is also borne in mind that

$$P_1 = p_1 + p_1^+ \tag{9}$$

$$P_2 = p_2 + p_2^+ \tag{10}$$

where P_1, p_1^+, and p_1 are the partial pressures of the total number of atoms, ionized, and neutral atoms of the test element respectively; P_2, p_2^+, and p_2 are the partial pressures of the total number of atoms, ionized, and neutral atoms of the influencing element; p_e is the partial electron pressure; K_1 and K_2 are the ionization constants of the test and influencing elements at a temperature of 2430°K.

The effect of the element introduced on the radiation intensity of the test element was calculated from the ratio of the number of its neutral atoms on adding KCl (or NaCl) to the number of neutral atoms for the case where no foreign elements are added, and also on the basis of the formula given in [30]:

$$I = CN(1 - X)e^{-E/KT}, \tag{11}$$

where X is the fraction of ionized atoms, C is a constant, N is the concentration of the element, and E is the excitation energy of the given line. The effect of the interference is given by:

$$\frac{i}{I_0} = \frac{1 - X}{1 - X_0}, \tag{12}$$

where X is the fraction of ionized atoms of the test element in the presence of the interfering element, and X_0 is the fraction of ionized atoms of the test element in the absence of any addition of interfering element.

The effects obtained experimentally and by calculation are compared in Tables 3-5.

Results of calculations show that the breakdown in the degree of ionization (Rb, Li, Na, Cs) which occurs on adding interfering elements KCl and NaCl can cause the effect which we have observed in our experiments.

It also follows from formula (5) that the effect of KCl on the radiation intensity of Rb, taken in equal amounts but in the form of different compounds, remains the same.

TABLE 3. Effect of 5000 mg KCl/liter on the Radiation Intensity of Li (670.8 mμ), Na (589.3 mμ), Rb (780.0 mμ), and Cs (852.1 mμ)

Test element, 10 mg/liter	5000 mg KCl/l introduced	
	I/I_0 experimentally determined	I/I_0 calculated
Li	0.99	1.0
Na	1.2	1.2
Rb	9.1	8.8
Cs	26.9	27.5

TABLE 4. Effect of the Same Amount of KCl and NaCl on the Radiation Intensity of Rb (780.0 mμ) for Varying Contents of the Latter

Rb taken, mg/liter	5000 mg KCl/liter introduced		5000 mg NaCl/liter introduced	
	I/I_0 experimentally determined	I/I_0 calculated	I/I_0 experimentally determined	I/I_0 calculated
10	9.1	8.8	5.2	5.1
20	5.2	5.3	3.7	3.6
30	3.8	3.9	2.5	2.3
40	3.6	3.5	2.5	2.1

TABLE 5. Effect of Various Amounts of KCl and NaCl on the Radiation Intensity of Rb (780.0 mμ) for a Constant Content of the Latter

KCl added, mg/liter	Test element Rb at a concentration of 10 mg/liter		NaCl* added, mg/liter	Test element Rb at a concentration of 10 mg/liter	
	I/I_0 experimentally determined	I/I_0 calculated		I/I_0 experimentally determined	I/I_0 calculated
5000	9.1	8.8	5000	5.2	5.1
500	6.1	6.4	500	2.8	2.7
50	2.6	2.8			

* We did not calculate the effect of low concentrations of NaCl (50 mg/liter) on the radiation intensity of Rb, since calculations of the partial pressure of neutral Rb atoms in the presence of the interfering element was carried out approximately under conditions such that $p^+_{interfering}$ was considerably greater than p^+_{test}; at an NaCl concentration of 50 mg/liter they would be similar.

SUMMARY

The mutual effect of the alkali elements has been studied. It has been found that addition of potassium chloride at the rate of 5000 mg/liter to test solutions of the other alkali elements (at contents of 10 mg/liter) does not alter the radiation intensity of Li, slightly increases the radiation intensity of Na, while it increases the radiation intensity of Rb nine times and that of cesium 27 times. On increasing the concentration of the interfering element KCl from 50 to 5000 mg/liter, the radiation intensity of rubidium increases (for a rubidium concentration of 10 mg per liter); the radiation intensity increases 2.6 times on adding 50 mg KCl/liter, and 9.1 times on adding 5000 mg KCl/liter. At equal concentrations of the interfering element (KCl 5000 mg/liter) but varying concentrations of Rb (10, 20, 30, 40 mg/liter) the interference effect decreases as the Rb concentration increases; for 10 mg/liter it is 9.1 while for 40 mg Rb/liter it is 3.6.

The results obtained can, apparently, be explained by the change in the degree of ionization of the atoms of the test element on adding to its solution another alkali metal. Calculations which have been made are in good agreement with experimental and theoretical data.

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THE INFLUENCE OF CERTAIN ORGANIC MATERIALS ON THE RADIATION OF CALCIUM IN A FLAME IN THE PRESENCE OF ALUMINUM

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Weakening of the radiation intensity of calcium and strontium in the presence of a number of metals, in particular aluminum, is well known [1-3]. The magnitude of this effect depends on the concentration of the interfering elements in solution; it changes on switching from one test material to another, and on reaching a significant value leads to serious interference during flame photometric determination of the alkaline earth elements. As a result it is necessary (particularly during the analysis of rocks and minerals) to remove aluminum, iron, and other elements, or compensate for their influence on the experimental results artificially [4,5].

Recently Debras-Guedon and Voinovitch [6] showed that addition of 8-hydroxyquinoline to the test solution permits the influence of aluminum on the line intensity of calcium to be reduced appreciably. They made use of this fact for determining the alkaline earth elements without preliminary removal of aluminum. The significant practical importance of the effect discovered led us to carry out a more systematic study of the effect of various organic compounds (including 8-hydroxyquinoline) on the results of the flame photometric determination of calcium. In the course of this work, on the basis of the results of a series of researches, and, in particular on the results of experiments with two atomizers [7], which showed that aluminum depresses calcium radiation only when both metals are present in the same solution (and does not show such influence when these elements are introduced separately into the flame), it was possible to conclude that the basic reason for the "extinction" of the calcium radiation by aluminum is the formation in the aerosol, at the moment when it is evaporating, of a difficulty volatile compound (possibly $CaAl_2O_4$) which does not break down during passage through the flame. If this is the case, then weakening or complete elimination of the effect of aluminum on the line intensity of calcium can be achieved by one of two methods: either by ensuring conditions such that aluminum at the point when the aerosol evaporates, forms some stable compound, or leads to formation in the aerosol of a sufficiently stable compound of calcium which would, however, be relatively easily destroyed in the flame. It is obvious that in the latter instance, the most suitable components which form compounds that readily break down in the flame, would be organic materials.

On this basis, in the work described here, we studied the effect of acetylacetone, 8-hydroxyquinoline, and also oxalic and salicylic acids.

The instability constants [8] of the complexes are: for $Al[Ox]^{3-}$ $-1.6\cdot10^{-17}$; and $AlSal^{3+}$ $-8\cdot10^{-15}$ and $Al[Acac]_3$ $-5.0\cdot10^{-23}$. Nevertheless, the experimental conditions were such that the corresponding aluminum complexes were not, apparently, formed in solution. The values of the instability constants for the corresponding complex compounds of calcium are unknown in most cases.

Experiments were carried out with an acetylene-air burner of the Mekker type provided with a separate atomizing chamber. The section of the flame at a distance of 5 mm from the inner cones were measured photometrically. The spectral apparatus used was an ISP-51 spectrograph with a FÉP-1 photoelectric apparatus and a recording galvanometer.

Results illustrating the effect of additions of various amounts of organic materials on the radiation intensity of the resonance line Ca 422.7 mμ, for solutions containing different amounts of aluminum are shown in Figs. 1-3. In order to get a complete picture, curves characterizing the effect of additions of the organic material on the radiation intensity of calcium* in the absence of aluminum are given at the same time on each of the curves.

* Experiments with strontium gave similar results.

Of great importance for clarifying the mechanism of the action of organic materials is the case of the effect of oxalate ions (Fig.1). Complexing of calcium ions by oxalate ions unfavorably affects the line intensity of calcium in the flame. The intensity gradually decreases with increasing oxalate ion concentration in solution. However, when the solution contains aluminum which is capable, under certain conditions, of forming more stable complexes with oxalate, in the presence of oxalate ions the calcium ions are prevented from forming a difficulty volatile chemical compound with aluminum, and under these conditions there is a significant increase in the intensity of the calcium spectral lines in the flame. While the oxalate concentration of the solution is still less than the equivalent concentration of aluminum, increases in the oxalate concentration promote complexing of increasing amounts of Al^{3+} ions and lead to a uniform increase in the line intensity of calcium (i.e., to a gradual and every increasing suppression of the "extinguishing" effect). When the oxalate concentration becomes equivalent to the aluminum concentration, the "extinguishing" effect of the latter on calcium reaches a minimum value, while the radiation intensity of calcium, correspondingly, becomes a maximum. Beyond this point there is observed a weakening in the line intensity of calcium caused by the "extinguishing" effect of the oxalate ion itself on calcium. The suggested mechanism which has been described for the action of oxalate ion on the "extinguishing" effect of aluminum with respect to the line emitted by calcium readily explains the shapes of all the curves given in Fig. 1. Since the maximum on these curves, in view of what has been said above, should be located near the equivalence point (denoted by dotted lines), this should enable one to get some idea of the composition of the complex formed in solution. According to our results, this complex has the formula $Al[C_2H_2O_4]^{3-}$ and is characterized [9] by an instability constant of 1.6×10^{-17}.

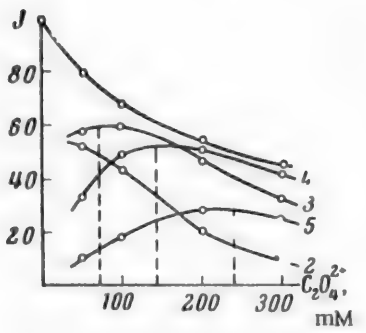

Fig. 1. Relationship between the intensity of the Ca line 422.7 and the concentration of oxalate ion for different aluminum concentrations and a constant calcium content (25 mg/liter). 1) Al, 0 mM; 2) Al, 10 mM; 3) Al, 20 mM; 4) Al, 40 mM; 5) Al, 50 mM.

Considerably less definite results were obtained during a study of the effect of salicylic acid (Fig. 2). Despite the fact that salicylic acid itself (in contrast to the case considered previously) does not exhibit an "extinguishing" effect on the line intensity of calcium, a maximum is observed again in this case on all the curves, the position of which shifts forward higher molar concentrations of salicylic acid as the aluminum concentration of the solution increases. Possibly, this indicates formation of one or more less stable aluminum complexes in solution during passage of the latter through the flame when excess salicylic acid is present. In order to confirm this, however, one must, of course, have direct proof.

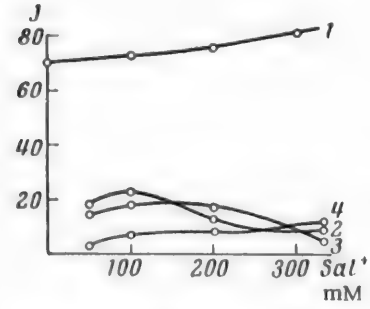

Fig. 2. Relationship between the intensity of the Ca line 422.7 and the concentration of salicylic acid for different aluminum concentrations and a constant calcium content (25 mg/liter). 1) Al, 0 mM; 2) Al, 15 mM; 3) Al, 30 mM; 4) Al, 120 mM

The most interesting results from a practical point of view were obtained during a series of experiments with acetylacetone and 8-hydroxyquinoline (Fig. 3). The effect of these compounds on the radiation intensity of calcium in the presence of aluminum is approximately the same. In their presence (Fig. 3), in both cases, the maximum intensity of the calcium lines is considerably greater than in the presence of the other materials tested (Figs. 1-2).

The fact that in both cases no "extinguishing" effect on the calcium line is observed on adding these compounds, leads to a smooth increase in the line intensity of this element as the concentration of the acetylacetone or 8-hydroxyquinoline in solution increases. The greater steepness of curve "a" as compared with curve "b" in Fig. 3 is explained by the fact that in contrast to experiments with acetylacetone, in solutions containing 8-hydroxyquinoline the viscosity simultaneously increases considerably with increasing concentration of this compound.* This should lead, as a consequence, to a relative decrease in the line intensity of calcium for solutions with a higher content of the organic compound. As is evident, the effect of additions of organic compounds on the line intensity of calcium depends on the aluminum concentration of the solution, so that complete elimination of the "extinguishing" effect

* Thus the viscosity of a 5% solution of 8-hydroxyquinoline is almost 1.5 times that of water. It should be emphasized that no precipitate of 8-hydroxyquinolate is formed under the experimental conditions used.

of aluminum, apart from its content, is, in general, not possible. We only observed such an effect in one instance when we introduced a 50% solution of acetylacetone in acetic acid (1:4) into the flame. Usually, however, in order to get correct results during determination of calcium in the presence of aluminum by the method indicated, one need only have an approximate idea of the aluminum content of the test solution. Matters are simplified during

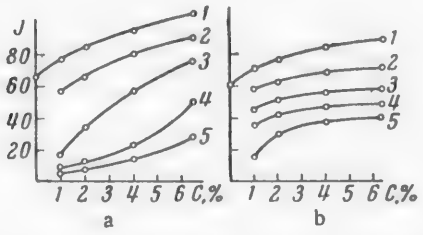

Fig. 3. The relationship between the intensity of the Ca line 422.7 and the concentration of acetylacetone (a) and 8-hydroxyquinoline (b) for different aluminum concentrations and a constant calcium content (25 mg/liter). 1) Al, 0 mM; 2) Al, 20 mM; 3) Al, 50 mM; 4) Al, 100 mM; 5) Al, 200 mM

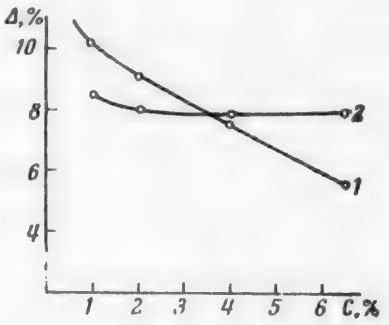

Fig. 4. The relationship between the value of the maximum experimental error in determining calcium, following upon a shift in the calibration curve in the presence of aluminum, and the concentration of 1) acetylacetone; 2) 8-hydroxyquinoline.

analysis of silicate rocks whose aluminum content does not usually exceed 20%. Without going into any details of the analytical technique, we should point out that on carrying out quantitative determination of calcium in rocks with the most diverse aluminum contents by means of calibration curves constructed with standards containing 0.25 mg aluminum/ml* as our experiments have shown, the maximum experimental error will vary with the content of added organic compounds within the limits indicated in the cruves in Fig. 4. The experimental error in determining calcium following from the presence of an unknown amount of aluminum in the sample can, if required, be considerably decreased by using a large number of standard solutions, the aluminum concentration of which would correspond to its concentration in the test rocks.

Results and conclusions similar to those made in the work described here with respect to aluminum and calcium, have also been obtained for other instances of "extinguishing" agents such as Ge, Ti and others, which, however, usually exhibit a much smaller influence on the flame photometric determination of the alkaline earth elements.

SUMMARY

A study has been made of the effect of a number of compounds capable of forming complexes with aluminum (oxalic acid, salicylic acid, 8-hydroxyquinoline, and acetylacetone) on the intensity of the spectral lines of calcium when the latter is determined by flame photometrically in the presence of aluminum. It has been shown that suppression of the "extinguishing" effect depends on the concentration of the organic compounds added, and on the aluminum content. A mechanism is suggested for the suppression of the "extinguishing" effect.

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*On the basis that a 250 mg aliquot dissolved in 100 ml it is used for determination of calcium and strontium.

PHOTOMETRIC DETERMINATION OF MAGNESIUM WITH THE REAGENT PICRAMINAZO

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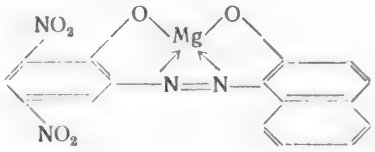
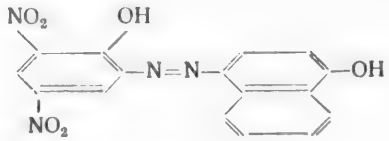
Most of the color reactions for magnesium are based on adsorption of various azo dyes and other materials by magnesium hydroxide during which the original color of the organic compound changes. In Kuznetsov's terminology [1] all these reactions are of the "colored solid phase" type. Azo- and diazo compounds having hydroxy- and nitro groups in the ortho or para positions with respect to the azo group are characteristic reagents for magnesium. Kul'berg [2] studied 25 azo dyes prepared by diazotization of p-nitroaniline. He has come to the conclusion that the change in the color of the dye during its interaction with magnesium ions in an alkaline medium is related to the development of an intracomplex compound. Kuznetsov showed that azo dyes with hydroxy and nitro groups in the ortho and para positions do not always give a color change with magnesium hydroxide. Moreover, there are a number of materials not containing the groups indicated, e.g. titanium yellow etc., which react with $Mg(OH)_2$. We completely share V. I. Kuznetsov's views regarding the mechanism of the interaction of magnesium with azo dyes and other materials in alkaline media, which is based on adsorption phenomena. We have examined azo dyes based on picramic acid; the molecular weight of these materials did not exceed 370-390. Without going into detail about all the experiments with azo dyes prepared for the first time, we should point out that on coupling diazotized picramic acid with α- and β-naphthols, compounds are formed which react with $Mg(OH)_2$ with an accompanying change in color. However, if Kul'berg's conclusions are correct [4], introduction of two hydroxy groups into the ortho position with respect to the azo group should sharply enhance the color of the reaction product as a result of the formation of an intracomplex compound;



this does not occur in actual practice. The azo dye obtained with β-hydroxynaphthol possesses low sensitivity to magnesium ions; on the other hand, coupling of diazotized picramic acid with α-naphthol gives a dye which permits detection of 0.25 μg Mg^{2+}/ml.

Below we give the results of a study of 2-hydroxy-3, 5-dinitro-1-azo-4, 1-hydroxynaphthalene (picraminazo)



as a potential reagent for magnesium during its determination in various materials, including biological materials. This reagent is a brown colored powder which is insoluble in acids and in cold water; it dissolves in ethanol, acetone, and caustic alkali solutions. The conditions used for determining magnesium by means of this reagent are similar to the conditions adopted for determination of magnesium by "phenazo" and titanium yellow. The caustic alkali concentration of the final solution is 1.5 N and higher. The absorption spectra of solutions of the reagent and of its compound with magnesium are shown in Fig. 1.

Picraminazo is readily synthesized and can be made in any laboratory.

Picraminazo permits determination of magnesium in the presence of up to 2000 times its amount of titanium in an alkaline solution, when the titanium is converted into peracid salts. Foreign ions which interfere are approximately those which interfere when previously suggested reagents are used. Interference from iron, manganese, zinc, and nickel cations can be eliminated by means of a solution of sodium diethyldithiocarbamate.

The sensitivity of the reaction with picraminazo for magnesium, according to Kuznetsov's microgram index [5,6] in extinction units is 0.022 at a wavelength of 580 mμ. This reagent therefore lies between phenazo and titanium yellow with respect to sensitivity [7]. F. M. and also FEK-M photometers can be used for magnesium determination by means of picraminazo, while the FÉK-M photometer cannot be used when the reagent adopted is magneson 1.

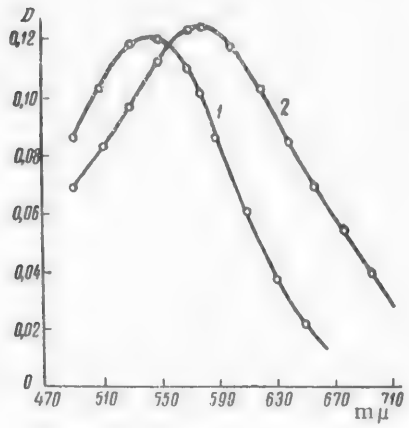


Fig. 1. Absorption of an alkaline solution of picraminazo (1) and with the magnesium hydroxide colored by it (2). Picraminazo solution 0.0000006 M; magnesium solution 0.00008 M; solution 1.8 N with respect to NaOH; path length of cell l = 20 mm.

A 0.005% ethanol solution of reagent was used for the photometric determination of magnesium. The solution can be stored without change for several months.

EXPERIMENTAL

Synthesis of Picraminazo Reagent. Five g of picramic acid was dissolved in 200 ml ethanol; hydrochloric acid (15 ml HCl sp.gr. 1.19 and 15 ml water) was then added to the solution. The mixture was cooled in ice. The calculated amount of 10% sodium nitrite solution was added slowly with careful stirring to the cooled solution. After 30 min the crystalline precipitate which had separated out was sucked off on a Buchner funnel; the precipitate was washed with a small amount of ice water, it was then transferred to a beaker and suspended in 50 ml of water. Twenty ml of a 10% ethanol solution of α-naphthol was added to the pasty mass. The mixture started to darken immediately and a dark-red color developed. To this mixture was added 10 ml of a saturated solution of Na_2CO_3. Fifty ml of acetic acid was added dropwise with stirring over a period of 3 hours and this was followed by 10 ml HCl (sp.gr. 1.19). The dye formed was heated on a boiling water bath, it was then filtered off and washed with a small amount of hot water. The material obtained was suspended in 500 ml of water, sodium hydroxide was added, and the solution obtained filtered free from insoluble residue; by acidifying the filtrate with hydrochloric acid the pure dye was separated out, the dye was then washed until the washing gave no reaction for chloride ion, and was finally dried at room temperature. A brick colored product was obtained; yield about 8 g.

Determination of Magnesium in Alloys

a) Cast Iron. An aliquot (about 1 g) of cast iron was dissolved on heating in hydrochloric acid (sp.gr. 1.19). The solution obtained was transferred to a 100 ml standard flask, diluted with water to the mark and the whole mixed. Ten ml of this solution was transferred to a 100 ml flask and neutralized with sodium hydroxide solution until the solution gave a blue-violet color with congo red paper; 20 ml of a 10% sodium diethyldithiocarbamate* solution was then added, the volume of the solution was made up to the mark with water and mixed. Part of the solution was filtered through a fine dry ashless filter paper into a dry flask. Ten ml of the filtrate was transferred to a 50 ml standard flask, 5 ml of 0.5% gelatin solution, 2 ml of 0.005% reagent solution, and 15 ml of 20% sodium hydroxide were added and the volume of the solution made up to the mark with water; the whole was mixed and the optical density measured on a FÉK-M photoelectric colorimeter using a red filter and a cuvette with l = 50 ml. Standard solution: 2 ml of 0.005% reagent solution, 5 ml of 0.05% gelatin solution, 15 ml of 20% sodium hydroxide solution, water to the mark in a 50 ml standard flask. Results of determinations are given in Table 1.

b) Titanium Alloys. An aliquot of alloy (1 g) was dissolved by Kuznetsov's method by heating it in 70 ml of hydrochloric acid (sp.gr. 1.19). The solution obtained was transferred to a 100 ml standard flask, diluted with water to the mark and mixed. A ten ml aliquot of this solution was pipetted into another standard flask (100 ml) and 20% sodium hydroxide solution added until the solution gave a blue-violet color with congo red paper. To the solution

* When this work was complete a short communication appeared in Zavodsk. laboratoriya, 21, No. 11 (1960) relating to the determination of magnesium in cast iron, in which the elements which interfere with this determination were precipitated beforehand with sodium diethyldithiocarbamate.

obtained after adding sodium hydroxide was added 20 ml of a 10% solution of sodium diethyldithiocarbamate and the solution diluted with water to the mark. Part of the solution was filtered through a fine dry filter paper. Ten ml of the filtrate was transferred to a 50 ml standard flask and the procedure outline above for cast iron analysis then followed.

During determination of magnesium in undegassed and degassed titanium, after the aliquot of titanium has been dissolved in hydrochloric acid, and the solution has been diluted with water until the total volume of the solution in the standard flask was 100 ml, 10 ml of the solution was transferred to a 50 ml standard flask; 0.5 ml of hydrogen peroxide, 5 ml of a freshly prepared and filtered 0.5% solution of starch, 2 ml of 0.005% reagent solution, and

TABLE 1. Determination of Magnesium in Iron Alloys by Means of Picraminazo

Alloy	Magnesium added, %	Magnesium found, %	Error, %	Alloy	Magnesium added, %	Magnesium found, %	Error, %
Magnesium free cast iron				Magnesium free cast iron			
No. 191	1.22	1.22	–	No. 193	0.3	0.32	+0.02
No. 191	1.22	1.19	-0.03	No. 193	0.6	0.58	-0.02
No. 192	1.00	1.00	–	No. 193	1.0	1.00	–
No. 192	1.00	1.00	–				

15 ml of 20% sodium hydroxide solution were added; the solution obtained was diluted to the mark with water. The optical density was measured after 10-15 min. The standard solution was prepared in the same way as that described for analysis of cast iron, the gelatin solution being replaced by starch solution. Results of determinations are given in Table 2.

TABLE 2. Determination of Magnesium in Titanium and Its Alloys

Test material	Magnesium content, %	Magnesium added, %	Magnesium found, %
Chemically pure titanium	–	0.5	0.50; 0.49; 0.51; 0.51
Undegassed titanium	0.47	–	0.47; 0.47
Undegassed titanium	0.47	0.5	0.96; 0.97; 0.95
Alloys based on titanium (VTZ-1)		0.2	0.2; 0.2; 0.19; 0.21; 0.51;
		0.5	0.50

c) Aluminum Alloys. An aliquot of alloy (0.2 g) was dissolved by V. I. Kuznetsov's method in 20 ml of 20% sodium hydroxide solution, the solution obtained was diluted with water to 150-200 ml and filtered through a fine paper, and the precipitated washed several times with 2% sodium hydroxide solution. The precipitate was dissolved on the filter with 10-12 ml of hydrochloric acid (sp.gr. 1.19), the solution being passed into a 100 ml standard flask. The filter was washed several times with hot water. The solution obtained was neutralized with sodium hydroxide until it gave a blue-violet color with congo red paper. Fifteen ml of 5% sodium diethyldithiocarbamate solution was added and the solution diluted with water to the mark. Ten ml of solution which had been filtered through a fine filter paper was transferred to a 50 ml flask. The analytical procedure that followed was the same as that for analysis of cast iron. Results are given in Table 3.

Determination of Magnesium in Water. 5-10 ml of water (depending on the expected magnesium contact) was pipetted into a 50 ml standard flask, 2 ml of 0.005% reagent solution, 5 ml of 0.5% gelatin solution, and 15 ml of 20% sodium hydroxide solution were added, and the volume of the solution made up to the mark; the whole was mixed. The optical density was measured after 10-15 min. Results for analysis of mineral waters are given in Table 4.

Determination of Magnesium in Biological Materials. 0.1-0.2 g of dried biological material (muscle, liver, spleen, etc.) was wet oxidized by the usual method in a Kjeldahl flask with sulfuric acid and hydrogen peroxide.

After complete break down, the solution was quantitatively transferred to a quartz basin and excess acid removed by evaporation. The residue was transferred to a 100 ml standard flask and neutralized with sodium hydroxide until the solution gave a blue-violet color with congo red paper. Twenty ml of 1% sodium diethyldithiocarbamate solution was added and the solution diluted to the mark with water and mixed. Part of the solution was filtered through a dry filter paper and 10-20 ml of the solution taken for analysis. The procedure described for analysis of cast iron was then followed. Results for air-dry materials are given in Table 5.

TABLE 3. Determination of Magnesium in Aluminum Alloys by Means of Picraminazo

Alloy	Specified magnesium content, %	Magnesium added to sample, %	Amount of magnesium that should be present, %	Magnesium found, %	Alloy	Specified magnesium content, %	Magnesium added to sample, %	Amount of magnesium that should be present, %	Magnesium found, %
Silumin 113a	0.065	0.25	0.315	0.315	Silumin No. 4	–	0.25	0.25	0.25
Silumin 113a	0.065	0.5	0.565	0.575	Silumin No. 4	–	0.5	0.5	0.5
Silumin No.3	0.035	0.25	0.285	0.285	Dural No.69-σ	0.67	–	–	0.68
Silumin No.3	0.035	0.375	0.41	0.385	Dural No.69-σ	0.67	–	–	0.69
Silumin No.3	0.035	0.500	0.535	0.535					

TABLE 4. Determination of Magnesium in Mineral Waters by Means of Picraminazo

Water	Specified magnesium content, mg/liter	Magnesium found by means of picraminazo	Water	Specified magnesium content, mg/liter	Magnesium found by means of picraminazo
Slavyanovskii	43.7	44	Smirnovskii	40.1	42.2
Bitautas	226	230	Batalovskii	1533	1500
Essentuki No. 20	89.1	88	Narzan	110	108
Izhev source	186	190			

TABLE 5. Determination of Magnesium in Biological Materials (White Rat)

Test material	Aliquot, g	Magnesium added, mg, %	Magnesium found, mg, %	Magnesium that should be present, mg, %	Deviation, mg, %
Spleen	0.1986	–	144.8	–	–
Spleen	0.2002	50	193.8	194.8	-1.3
Blood clots	0.0918	–	103.5	–	–
Blood clots	0.0922	40	140.9	143.9	-2.6
Liver	0.1900	–	92.1	–	–
Liver	0.1986	50	142.3	142.1	+0.2

SUMMARY

A new reagent for magnesium called picraminazo has been synthesized. The reagent possesses a high sensitivity.

Photometric methods have been developed for determination of magnesium in cast iron, titanium and its alloys, alloys based on aluminum, mineral water, and biological materials. All the methods are reasonably simple and accurate and take comparatively little time.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

PHOTOMETRIC DETERMINATION OF THE CALCIUM CONTENT OF CEMENT MATERIALS BY MEANS OF COMPLEXONS

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Photometric methods of determining SiO_2, Al_2O_3, and Fe_2O_3 [1] in raw materials and finished products are widely used in many cement plants. It would be expedient to develop a photometric method for the determination of CaO, particularly since visual complexometric titration of calcium is complicated by the fact that the color change of the indicator at the end point is not clear enough.

There is very little information on photometric methods of determining calcium. Thus Sandell [2] recommends two indirect methods for the photometric determination of calcium after it has been precipitated. Marti et al. [3] have determined microamounts of calcium on the basis of the weakening of the color of an iron salicylate solution by sodium oxalate remaining in excess after precipitation of calcium ions. A method exists which is based on decolorization of chloranilic acid by calcium salts [4]. The method requires removal of the precipitate of calcium chloranilate and uses a reagent which is not readily available. Murexide has been used in some papers [5,6] for photometric determination of calcium. Nevertheless, the dye is not very stable (not more than 8 hr) even in ethanolic solution, and the optical density of the solutions must be measured within 5 min. In addition, iron, manganese, cobalt, and certain other ions interfere with the determination when they are present in solution.

Calcium [7] which was recently synthesized both for the titrimetric and photometric determination of calcium has some essential drawbacks: the experimental results depend to a large measure on the salt concentration of the solutions which are being photometrically measured; this excludes the possibility of using this reagent for the analysis of cement materials.

All the methods outlined above are applicable for the determination of not more than 5-10% Ca, whereas the calcium content of cement materials amounts to 40-70%.

As the foundation of the method which we should like to suggest for the determination of high contents (40-45% Ca) we set a method based on complexing most of the calcium as a colorless complex and obtaining a colored compound with the remaining free calcium ions (amounting to 5-6%). This allows the accuracy with which calcium is determined to be increased by one order. Such a method is suitable for series of samples, in which the concentration of the test element varies within the limits 5-6%. Thus during determination of calcium in raw mixes it is possible to complex 40% of it into a stable complex with sodium ethylenediaminetetracetate (EDTA-Na), so that only the remaining 2-5% of the calcium ions will participate in formation of the colored compound. This is possible because the instability constant of calcium ethylenediamietetracetate is significantly less than with metallo indicators. As a result it is possible to attain an absolute error of 0.2-0.3% for such amounts of calcium.

Formation of a compound between calcium ions and acid chrome dark-blue was chosen for the photometric determination of calcium. Aqueous solutions of acid chrome-dark-blue are stable for several weeks. We had to abandon the use of murexide because of the insufficient stability of even its ethanolic solutions. Eriochrome black T is also unstable in the presence of masked sesquioxides.

In studying the conditions for the formation of the colored compound of calcium with acid chrome dark-blue in pure solutions of calcium, and in the presence of other cations, it was necessary to follow the character of the absorption of light by these solutions, to establish the optimum concentration of the dye, alkali, EDTA-Na, and triethanolamine, and to check on the absence of interference on the part of magnesium, iron, and aluminum.

The preliminary experiments and construction of calibration curves were carried out with pure solutions of $CaCl_2$ in 0.5 N HCl containing 0.12 mg CaO/ml, corresponding to a content of 2% CaO in the samples on taking an aliquot of 0.15 g, diluting to 500 ml, and taking a 20 ml aliquot of the solution.

In the presence of calcium ions, acid chrome dark-blue has a red color, while in their absence the color is violet-blue. The sensitivity of acid chrome dark-blue for calcium ions at pH 9-13 is 1.4×10^{-7} g/ml, while for magnesium ions the sensitivity of this dye is 2×10^{-8} g/ml.

To attain the highest concentration sensitivity it is necessary to choose definite wavelength for measuring the optical density of the solutions. In order to do this we studied the absorption curves of a 0.02% aqueous solution of the free reagent in the presence of 1.7 mg of calcium completely complexed with EDTA-Na, and of solutions containing the reagent uncomplexed calcium ions in amounts of 100 and 275 μg in excess of the amount of calcium given above. The conditions used for obtaining the colored solutions are given below.

As Fig. 1 shows, the largest difference in optical densities corresponds to a wavelength of 600 mμ; i.e., measurement of the optical density of the solutions must be carried out with a yellow filter (λ_{max} = 595 mμ), and on the basis of the weakening of the dye color. Ten ml of a 0.02% aqueous solution of the reagent is added; under these conditions the change in optical density occurs in the most favorable part of the scale of the apparatus for experimental work, and a sufficiently high accuracy is ensured.

Calcium is determined photometrically in a strongly alkaline medium at pH ≥12; under such conditions magnesium is precipitated as its hydroxide and does not react with acid chrome dark-blue the residual magnesium concentration is 10^{-11} g/ml which is significantly lower than the sensitivity of the reagent for magnesium. As a result it is possible to determine calcium in the presence of magnesium when the pH of the solution has the appropriate value [8].

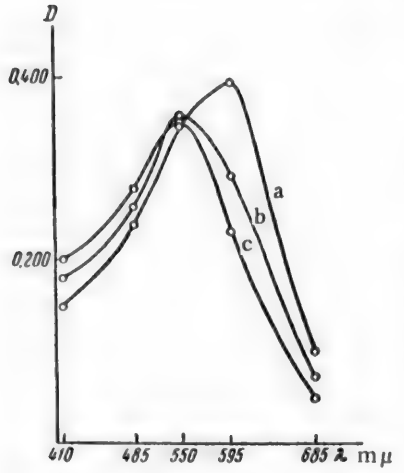

Fig. 1. Absorption curves of solutions of acid chrome dark-blue (a), and of solutions of its complexes with various amounts of calcium: b) 100 μg; c) 275 μg.

The optimum concentration and the amount of alkali added were established by examining the effect of various amounts of NaOH on the position and nature of the calibration curves for pure solutions of calcium.

A calibration curve was constructed by introducing 20 to 23 ml of standard $CaCl_2$ solution at 0.5 ml intervals into 100 ml standard flasks; these amounts of standard solution corresponded to CaO concentrations in the raw mixes of 40 to 46% in 1% intervals. Twenty ml of 0.00450 M EDTA-Na solution was then added to each flask; this complexed the same amount of calcium (about 40%) into a stable colorless complex. The solutions were made alkaline with 5 ml of NaOH of the following concentrations: 5, 10, 15, and 30%. Ten ml of dye solution was added, and the volumes made up to the mark with water. The optical density of the solutions obtained was measured on a FEK-M apparatus using a 10 mm cell and a yellow filter. The color of the solution is stable for 30 min. The calibration curves (Fig. 2) confirm the reversibility of the complex forming reaction: with increasing CaO and NaOH concentration there is a shift in the equilibrium as a result of which the lines become curves and the Lambert-Beer law is no longer obeyed.

In addition, increases in the alkalinity lower the slope of the curves and lead to a decrease in sensitivity. Five ml of a 10% NaOH solution can be regarded as the optimum amount. Further decreases in alkalinity significantly increase the dependence of the optical density on variations in pH.

A 1% aqueous solution of triethanolamine (TEA) for masking iron and aluminum was used during a study of the effect of magnesium, aluminum, and iron on the results of calcium determination. More complete and stable masking of aluminum was realized by introducing 0.5% sodium fluoride into the TEA solution. Five ml of the prepared mixture was added. At the same time we examined the effect of standing the test solutions for 10 min after addition of 5 ml of alkali to them.

On the basis of the results obtained (Table 1) it can be concluded that during analysis of samples containing up to 5% MgO and 10% Al_2O_3 one need not leave the solutions to stand. In the case of samples with a higher magnesium content the alkali solutions must be allowed to stand for 10 min for preliminary formation of a magnesium precipitate. Sodium fluoride must be added whatever conditions are used.

We were unable to eliminate interference when 0.36 mg of magnesium and 0.63 mg of aluminum were present in 100 ml of the final solution. Iron, even in amounts of 1 mg, did not interfere with calcium determination.

Since the content of calcium and sesquioxides in cement materials is considerably lower than the established limits, there is no interference from the sesquioxides during photometric determination of calcium (Table 2).

The mean square error is 0.1%.

The analytical conditions used were as follows. A 0.15 g aliquot of sample was fused with 1 g of fusion mixture (one part borax, two parts soda). The melt was dissolved on continuous stirring in 100 ml HCl (1:3) and the solution

TABLE 1. Effect of Magnesium, Iron, and Aluminum on the Results of Calcium Determination

Experimental conditions	Absolute systematic error (%) in the determination of the percentage content of CaO in the presence of:									
	MgO, %				Fe_2O_3, %		Al_2O_3, %			
	5	8	10	15	15	20	5	10	15	20
Without NaF, and without allowing to stand	+0,65	+1,05	—	—	0,0	—0,10	+0,55	+2,0	+2,82	—
Allowed to stand for 10 min	0,0	+0,30	+0,60	+0,90	—0,15	+0,09	—0,22	+0,18	+0,44	+0,70
With NaF, and without allowing to stand	+0,25	+0,75	—	—	0,0	+0,18	0,0	+0,14	+0,22	+0,38
Allowed to stand for 10 min	0,0	+0,05	+0,40	+0,55	—0,03	+0,05	+0,06	—0,12	—0,20	—0,34

TABLE 2. Comparative Results for the Photometric and Titrimetric Methods of Determining CaO in Cement Materials

Sample	CaO content, %					
	titrimetric method	photometric method				deviation (absolute), %
Standard raw mix	42.70	42.67	42.74	42.81	42.74	+0.04
Leningrad plant raw mix	43.26	43.20	43.24	43.13	43.19	-0.07
Spasskii plant raw mix	44.65	44.89	44.72	44.72	44.78	+0.13
Rizhskii plant raw mix	43.45	43.39	43.28	43.37	43.38	-0.07
Pikalevskii plant clinker	61.30	61.26	60.96	61.38	61.20	-0.10
Bryanskii plant clinker	66.28	66.02	66.20	66.08	66.10	-0.1
Volkhovskii plant clinker	65.45	65.59	65.49	65.26	65.45	0.08
Irkutsk plant clinker	63.31	63.25	63.49	63.33	63.38	+0.08

transferred to a 500 ml standard flask; the volume of the solution was then made up to the mark with water. After mixing, a 20 ml aliquot was transferred into a 100 ml standard flask, and 5 ml of the mixture of 1% TEA solution containing 0.5% NaF added; this was followed by 20 ml of 0.00450 M EDTA-Na solution. The solution was next neutralized with 10% NaOH using methyl red as indicator and an excess of 5 ml of alkali was then added. After addition of 10 ml of dye solution, the volume was made up to the mark with water. The mixed solution was measured photometrically. The percentage content of CaO was determined on the basis of the extinction value.

At the same time a solution of a standard raw mix with a known CaO content, as determined by several methods, was examined, with the aim of introducing corrections for changes in the photometric conditions from those used for constructing the calibration curve; the changes are usually accompanied by parallel displacements of the calibration curve. This was carried out as follows: when, under the new conditions, but using a calibration curve constructed earlier, we found a CaO content in the standard raw mix which was, e.g., 0.3% higher than it should be, this value was subtracted from the CaO content found for the test sample, while if the CaO content was 0.3% lower, then this value was added.

Analysis of samples of raw mixes and clinkers was carried out using the same calibration curve. Only 0.1 g of clinker was taken for analysis; results of the determinations increased 1.5 times. A concentration range of 61 to 67% was covered.

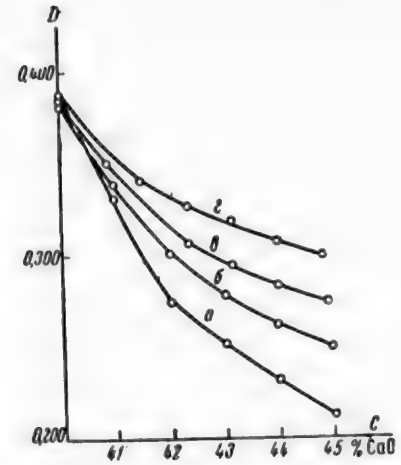

Fig. 2. Effect of the alkalinity of calcium solutions on the position and the nature of the calibration curves on adding NaOH of the following concentrations: a) 5%; b) 10%; c) 15%; d) 30%.

During clinker analysis corrections were initially applied, subsequently the results were multiplied by 1.5.

Determination of CaO, without taking into account fusion and dissolution, takes about 15 min.

Chemically pure or analytical grade calcium carbonate or standard sample of raw mix can be used for constructing the calibration curve; these materials should be taken through all the same analytical operations as the test samples.

SUMMARY

A photometric method is suggested for the determination of high concentrations of calcium which does not involve separation of sesquioxides; the method is based on complexing most of the test calcium with EDTA-Na into a colorless complex and on formation of a colored compound with the remaining free calcium ions. The error does not exceed ≠0.3% (absolute) for calcium contents in cement mixtures ranging from 40 to 45%, and in clinkers from 60 to 67%. A single determination, excluding fusion and dissolution of sample, takes about 15 min.

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DETERMINATION OF CERIUM IN CAST IRON BY TITRATION WITH HYDROQUINONE SOLUTION

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We have developed a reliable and comparatively rapid method for determining cerium in ferrous metals. It consists of: a) separating cerium as its fluoride from other elements at pH 2-5; b) rapid and accurate titrimetric determination of cerium with hydroquinone solution.

It is often recommended that the main element be removed by electrolysis with a mercury cathode [1]; this method, however, is not very convenient for plant laboratories; precipitation of cerium as its periodate [2], oxalate [3], and iodate is not applicable to the analysis of cast iron. The solubility product of CeF_3 as determined radiometrically is 8.1×10^{-16}, while the value determined conductometrically is 1.1×10^{-15} [4]. According to the results of the same authors the solubility of cerium fluoride depends on the pH of the solution, thus at pH 2 it is equal to 3×10^{-5} M, while at pH 1 it is 1.2×10^{-4}M, and at pH 0 it is 1.1×10^{-3} M. Ferric ions should be absent, since they bind fluoride ions into a stable complex, while in the presence of ferrous iron a precipitate of $FeF_2.FeF_3$ [5] is given; accordingly, before precipitating the CeF_3, ascorbic acid is added to the solution to prevent oxidation of ferrous iron.

The precipitate of the fluorides is filtered off, washed, and after ashing, treated with sulfuric acid to remove HF completely; in this way a solution of the sulfate of the rare earth elements is obtained which is almost free from impurities. An aliquot of cast iron containing 2-3 mg of cerium is taken and it is best to determine such an amount titrimetrically. Volodarskaya [6] recommends that cerium be oxidized to its quadrivalent state by ammonium persulfate (without using silver nitrate) and that titration be carried out with 0.02 N ferrous sulfate in the presence of ferroin. A hydroquinone solution, however, possesses appreciable advantages as a reducing agent [7]. Although the redox potential of the system hydroquinone–quinone (0.681 v) is higher than that of other systems (ascorbic acid, +0.43 v; stannous chloride, +0.2 v), hydroquinone is convenient in that at normal temperature, in acid solution, it immediately and quantitatively reduces quadrivalent cerium, and also iodide, bromide, chloride, bromate, chromate, and vanadate. A solution of hydroquinone in 1-3% sulfuric acid is stable on storage.

Ferroin or diphenylamine can be used as indicators but the former is preferable.

Cerium can be determined with reasonable accuracy in the presence of lanthanum, neodymium, and praseodymium by means of hydroquinone. Trivalent iron and sexivalent molybdenum do not interfere at contents less than 5 mg; at higher contents of these ions positive errors are obtained. Vanadates and chromates also interfere.

Determination of Cerium in Synthetic Mixtures. Cerium sulfate solution was standardized gravimetrically using the oxalate method.

The solution of hydroquinone (0.005 N) in 1% sulfuric acid was standardized against ceric sulfate solution.

A 0.025 M solution of indicator, o-phenanthroline–ferrous sulfate (ferroin), was used.

150 ml of water was added to 10 ml of cerium sulfate solution contained in a 250 ml flask, 5 ml of sulfuric acid sp.gr. 1.84 was added and the cerium oxidized with 25% ammonium persulfate solution. After oxidation, the solution was boiled for 5-7 min (until excess oxidizing agent had been completely destroyed) and then cooled. The quadrivalent cerium in the cooled solution was titrated with 0.005 M hydroquinone, after addition of one drop of ferroin, until a rose color appeared.

Experiment No. 1. Ten ml of cerium salt solution was taken (T_{Ce} = 0.000400 g/ml). Titration results and their statistical treatment are given in Table 1.

$\bar{x} = 4.000 - \frac{1.1 \cdot 10^{-1}}{7} = 4.000 - 0.016 = 3.984$: $\Sigma (x_i - \bar{x})^2 = 4.3 \cdot 10^{-3} - 7 \cdot (4.000 - 3.984)^2 = 4.3 \cdot 10^{-3} - 7 \cdot (0.016)^2$ $= 2.5 \cdot 10^{-3}$; $S^2 = \frac{2.5 \cdot 10^{-3}}{6} = 0.41 \cdot 10^{-3}$; $S_x = \frac{2.5 \cdot 10^{-3}}{7.6} = 7.7 \cdot 10^{-3}$; $= t_1 = \frac{4.000 - 3.984}{7.7 \cdot 10^{-3}} = \frac{16 \cdot 10^{-3}}{7.7 \cdot 10^{-3}} = 2.1$

which gives a reliability of $\alpha = 0.93$.

TABLE 1.

x_i, ме	$(x_i - 4) \cdot 10^3$	$(x_i - 4)^2 \cdot 10^3$
4,00	0	0
4,00	0	0
4,00	0	0
3,97	—3	9
3,95	—5	25
3,97	—3	9
4,00	0	0
Total	$-1,1 \cdot 10^{-1}$	$4,3 \cdot 10^{-3}$

It is possible to say therefore with a probability of 0.93 that the accuracy which can be reached for cerium determination is $\pm 2.1 \cdot 7.7 \cdot 10^{-3}$ $= \pm 15.7 \cdot 10^{-3}$ mg, or 0.4% (relative).

Experiment No. 2. Ten ml of cerium salt solution taken ($T_{Ce} = 0.000171$ g/ml).

Five determinations were carried out.

Results of statistical treatment are as follows:

$$\bar{x} = 1,7\ 7 \text{ mg}; \quad \Sigma (x_i - x)^2 = 0,8 \cdot 10^{-4};$$

$$S^2 = \frac{0,8 \cdot 10^{-4}}{4} = 0,2 \cdot 10^{-4}; \quad S_x = \sqrt{\frac{0.8 \cdot 10^{-4}}{4 \cdot 5}} = 2 \cdot 10^{-3};$$

$$t_1 = \frac{1,717 - 1,710}{2 \cdot 10^{-3}} = 3,5; \quad \alpha = 0,97.$$

The experimental accuracy is: $\pm 2 \cdot 10^{-3} \cdot 3.5 = \pm 7 \cdot 10^{-3}$ mg, or 0.4% (relative).

Experimental No. 3. Ten determinations of cerium were carried out in solutions with increasing cerium contents from 0.6 to 15 mg.

The statistical treatment of the results is given in Table 2.

TABLE 2.

Ce taken x_i, mg	0,60	1,200	1,710	1,800	2,400	3,000	4,000	6,000	9,000	15,000
Ce found y_i, mg	0,598	1,199	1,717	1,788	2,395	2,974	3,984	6,017	9,040	14,980
$\frac{y_i}{x_i} = z_i$	0,9866	0,9991	1,0041	0,9933	0,9980	0,9913	0,9960	1,0026	1,0044	0,9987
$(z_i - \bar{z}) \cdot 10^3$	—10,8	+1,7	+6,7	—4,1	0,60	—6,1	—1,4	+5,5	+6,8	+1,330
$(z_i - \bar{z})^2 \cdot 10^5$	11,66	0,289	4,489	1,681	0,036	3,721	0,196	2,916	4,624	0,169

The following values were calculated from the results given in this table.

$\Sigma z_i = 9,9743$ $\quad \bar{x} = 4,471$

$\Sigma x_i = 44,71$ $\quad \bar{y} = 4,468$

$\Sigma y_i = 44,681$ $\quad \bar{z} = 0,9974$

$\Sigma x_i y_i = 380,670$ $\quad \Sigma (x_i - \bar{x})^2 — 180,028$

$\Sigma (x_i)^2 = 380,72$ $\quad \Sigma (z_i = \bar{z})^2 = 3,005 \cdot 10^{-4}$

$\Sigma (y_i)^2 — 380,484$

The relation between the amount of cerium taken and that found is expressed by the equation for a straight line:

$$y = a + bx$$

where a is the value of the intercept on the ordinate and b characterizes the slope of the line to the abscissa.

The coefficients are calculated as follows [8, 9]:

$$b = \frac{n\Sigma x_i y_i - \Sigma x_i \Sigma y_i}{n\Sigma (x_i)^2 - (\Sigma x)^2} = \frac{10 \cdot 380,670 - 44,71 \cdot 44,681}{10 \cdot 380,72 - (44,71)^2} = 0,9993;$$

$$a = \overline{y} - b\overline{x} = \frac{\Sigma y_i - b\Sigma x_i}{n} \quad \frac{44,681 - 0,9993 \cdot 44,71}{10} = 0,0003.$$

Thus the relation between x and y is expressed by the equation for a straight line in the form

$$y = 0.9993x + 0.0003$$

$Y_{calc.}$, $y_i - Y_{calc.}$, $(y_i - Y_{calc.})^2$ and $\Sigma (y_i - Y_{calc.})^2$ are calculated by means of this equation. These values are given in Table 3.

TABLE 3.

$Y_{calc.}$	0,5999	1,199	1,698	1,799	2,399	2,998	3,997	5,996	8,994	14,990
$y_i - Y_{calc.} \cdot 10^3$	7,9	0	12	—11	—4	—24	—13	21	46	—10
$(y_i - Y_{calc})^2 \cdot 10^5$	6,2	0	14,4	12,1	1,6	57,6	16,9	44,1	212,6	10

From which $\Sigma(y_i - Y_{calc.})^2 = 3.68 \times 10^{-3}$;

$$S_y = \sqrt{\frac{\Sigma (y_i - Y_{calc})^2}{n-2}} = \sqrt{\frac{3,68 \cdot 10^{-3}}{8}} = 2,2 \cdot 10^{-2};$$

$$S\left(\text{from the ratio } \frac{y_i}{x_i}\right) = \sqrt{\frac{3,005 \cdot 10^{-4}}{9}} = 0,6 \cdot 10^{-2};$$

$$Sa = S\sqrt{\frac{\Sigma x_i^2}{n\Sigma x_i^2 - (\Sigma x_i)^2}} = S\sqrt{\frac{380,72}{10 \cdot 380,72 - (44,71)^2}} =$$

$$= 0,6 \cdot 10^{-2} \cdot 0,46 = 0,27 \cdot 10^{-2}; \; Sa = 0,27 \cdot 10^{-2}.$$

$$Sb = \frac{S}{\Sigma x_i^2 - \overline{x}\Sigma x_i} = \frac{0,6 \cdot 10^{-2}}{\sqrt{380 \cdot 72 - 4,471 \cdot 44,71}} = \frac{0,6 \cdot 10^{-2}}{13,42} = 0,45 \cdot 10^{-3}; \; Sb = 0,45 \cdot 10^{-3}.$$

Results of the statistical treatment show that the straight line expressing the relationship between the amount of cerium taken and that found by our method, passes through the origin, i.e., there is no systematic error.

The slope found for the straight line (0.9993) is in good agreement with z (0.9974), accordingly, the suggested method possesses adequate precision.

Determination of Cerium in Cast Iron. A 1-3 g aliquot of cast iron (depending on the cerium content) is introduced into a 250 conical flask; 25-30 ml of HCl (1:1) is added and the whole heated until the aliquot has dissolved completely. The solution is filtered free from graphite into a 100 ml conical flask. The volume of filtrate plus washing should not exceed 50 ml. 0.5 g of ascorbic acid is added to the cold solution to reduce trivalent iron, and 25% ammonia solution added dropwise to incipient precipitate formation. 0.5 g of sodium fluoride is added, and, after the flask has been sealed with a tight fitting rubber stopper, its contents are vigorously shaken for one hour (mechanical shaking).

The precipitate of fluorides are filtered off on a fine filter and washed 4-5 times with hot water. Filter plus precipitate are placed in a porcelain crucible; they are ignited and calcined gently in a muffle at not too high a temperature.

The calcined residue is transferred from the crucible into a 250 ml flask. 15 ml of sulfuric acid (1:4) is added and the liquid evaporated to the appearance of thick white fumes of SO_3 in order to remove fluoride completely. The

cooled residue is dissolved in 150 ml of water, a further 5 ml of sulfuric acid sp.gr. 1.84 is added and the cerium oxidized with 10-25 ml of 25% ammonium persulfate. The whole is boiled for 5-7 min for complete removal of excess oxidizing agent. One drop of ferroin solution is added to the cooled solution and titration carried out with 0.005 N hydroquinone solution to the appearance of a rose color.

We have adopted this method in our laboratory for analyzing modified cast iron.

Results of the analysis of three samples of cast iron are given to characterize the method (Tables 4 and 5):

TABLE 4.

Sample no.	% Cerium according to each determination					
1	0,0538	0,0538	0,0545	0,0545	0,0538	0,0561
2	0,0608	0,0608	0,0592	0,0592	—	—
3	0,0910	0,0906	0,0906	0,0916	0,0910	—

TABLE 5.

	Sample			Total
	№ 1	№ 2	№ 3	
No. of determinations Ni	6	4	5	15
Sum of results multiplied by 10^4 ($x_i = 10\,000\,x_i$) Σx_i	3265	2400	4548	
Σx_i^2	1 777 103	1 440 252	4 136 928	
$\frac{(\Sigma x_i)^2}{Ni}$	1 776 661	144 000	4 196 861	
$\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{Ni}$	442	252	67	761

$$S' = \sqrt{\frac{761}{15-3}} \simeq 8$$

$$S = 0{,}0008\%$$

The results were treated statistically by Doerffel's method [10].

At a confidence level of 0.95 and 12 degrees of freedom, t = 2.19, i.e., in five cases in a hundred, the deviation of the percentage content found will be greater than 2.19 × 0.008% = 0.0017%.

SUMMARY

A simple method is suggested for the quantitative separation of cerium by means of sodium fluoride.

A rapid titrimetric method for the determination of cerium by means of a solution of hydroquinone is suggested. Statistical treatment of the analytical results shows the absence of any systematic error, and demonstrates the high accuracy of the results.

Determination of cerium by the suggested method takes 5-6 hr.

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DETERMINATION OF TITANIUM IN TITANIUM CARBIDE-VANADIUM ALLOYS

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Vanadium is known to interfere with the titrimetric and gravimetric determination of titanium. Fusion with sodium peroxide or with a mixture of sodium carbonate and potassium carbonate, with subsequent leaching of the melt with water, and also precipitation of titanium with sodium hydroxide and sodium carbonate [1,2] have been used for separating titanium and vanadium. At high vanadium contents, titanium is determined after removal of vanadium by distillation in a stream of hydrogen chloride. In the course of analyzing alloys of titanium carbide and vanadium metal, at vanadium contents greater than 30%, we checked on the fusion method with sodium peroxide subsequent leaching of the melt with water and double precipitation with sodium hydroxide. It was established in the course of this work that complete separation of titanium and vanadium cannot be achieved.

In order to separate titanium and vanadium we precipitated the latter with sodium diethyldithiocarbamate in the presence of masking agents. Both vanadium and titanium are known to form compounds with diethyldithiocrabamate which are sparingly soluble in water [3]. Chernikhov and Dobkina [4] have shown that vanadium diethyldithiocarbamate has a high stability in acid solutions. It is not formed in neutral or weakly alkaline solutions. Vanadium diethyldithiocarbamate is readily extracted by organic solvents, the best extractant in acid solutions being chloroform. Extraction of vanadium from the chloroform extract into the aqueous phase is achieved by shaking with nitric acid in the presence of hydrogen peroxide or hydrochloric acid. The method of removing vanadium from titanium by precipitating it with diethyldithiocarbamate in the presence of citric acid is recommended for the photometric determination of titanium in heat resistant alloys [5].

The aim of the work described here was a detailed study of the possibility of separating titanium and vanadium by precipitation with diethyldithiocarbamate in the presence of various masking agents. According to Pyatnitskii [6] vanadium is completely masked by tartaric acid at pH 7, and by citric acid at pH 4, 5 when a 50-fold amount of each of the acids is used. Titanium is not precipitated by diethyldithiocarbamate whatever the pH, either in the presence of tartaric or citric acids.

The problem confronting us was the direct opposite of that solved by I. V. Pyatnitskii; we had to find the pH at which vanadium would be completely precipitated by diethyldithiocarbamate in the presence of tartaric, oxalic, and citric acids and fluorides. The complex compounds of titanium with tartaric, oxalic, and citric acids, and fluorides are not decomposed by diethyldithiocarbamate, and titanium can be determined in the aqueous phase in the presence of the materials listed.

The following experiments were carried out in order to establish the pH for complete precipitation of vanadium with diethyldithiocarbamate in the presence of the masking agents. To a sulfuric acid solution of vanadium containing from 0.1-0.15 g of the latter was added masking agent in an amount 20 times that of the vanadium; the pH was adjusted to the requisite value by addition of ammonia, acetate-ammoniacal buffer of the appropriate pH value and dry sodium diethyldithiocarbamate were then added. The vanadium diethyldithiocarbamate precipitate was extracted with chloroform. The vanadium content of the aqueous phase was determined photometrically with hydrogen peroxide in the presence of sodium fluoride.

The results obtained (Table 1) show that vanadium is quantitatively precipitated with diethyldithiocarbamate in the presence of tartaric acid at pH 3-5, in the presence of citric acid at a pH not higher than 3, and in the presence of fluorides at pH 5.6. In the presence of oxalic acid vanadium remains in the aqueous phase whatever the pH, although at pH 5-6 these amounts are insignificant.

In order to check on the possibility of separating titanium and vanadium by precipitation with sodium diethyldithiocarbamate in the presence of masking agents, synthetic mixtures with the following Ti:V ratios were prepared 1:0.5, 1:1, 1:1.5. The amount of titanium was the same in all the experiments, namely 0.1 g. Appropriate amounts

TABLE 1. Effect of the pH of the Solution on Precipitation of Vanadium with Diethyldithocarbamate in the Presence of Masking Agents in Amounts which are 20-times that of the Vanadium

Masking agent	Tartaric acid				Citric acid				$H_2C_2O_4$				NH_4F			
pH of the solution	3	4	5	6	2.5	3	4	5	3	4	5	6	3	4	5	6
No. of extractions with chloroform	1	1-2	2-3	5-6	1-2	1-2	2-3		3-4	3-4	3	2-3	3-4	3-4	2-3	2-3
Color of the aqueous phase after extraction	colorless			traces	colorless		traces		light blue, blue	light blue	colorless		light blue		colorless	
Amount of vanadium in the aqueous solution, %	0	0	traces	5-10	0	traces	5-10		10-20	5-10	2-5	1-2			0	0

TABLE 2.

Masking agent	Amt. of titanium, g	Vanadium added, g	pH of the solution	Ti found, g	Error (absolute)	Error (relative) %
Tartaric acid	0,1104	0,0512	3—4	0,1107	+0,0004	0,3
	0,1104	0,0512	3—4	0,1110	+0,0006	0,5
	0,1104	0,1023	3—4	0,1105	0,0001	0,1
	0,1104	0,1023	3—4	0,1107	0,0001	0,2
	0,1104	0,1533	3—4	0,1101	—0,0003	0,3
	0,1104	0,1573	3—4	0,1105	+0,0001	0,1
	0,1125	0,0512	5	0,1188	0,0065	5,5
	0,1125	0,0512	5	0,1160	0,0035	3
	0,1125	0,1023	5	0,1183	0,0065	5,5
	0,1125	0,1533	5	0,1170	0,0045	4,0
	0,1125	0,1533	5	0,1165	0,0040	3,5
Citric acid	0,1104	0,1023	3—4	0,1145		3,5
	0,1104	0,1023	3—4	0,1168		6,0
	0,1104	0,1533	3—4	0,1150		4,0
	0,1104	0,1533	3—4	0,1145		3,5
Oxalic acid	0,1104	0,0512	5—6	0,1111		0,6
	0,1104	0,1023	5—6	0,1143		3,0
	0,1104	0,1023	5—6	0,1132		2,5
	0,1104	0,1023	5—6	0,1135		3,0

of masking agent were added to sulfuric acid solutions of Ti and V, the pH was adjusted to a definite value, and the vanadium diethyldithiocarbamate extracted. Titanium was determined in the aqueous phase either titrimetrically or gravimetrically.

As the results obtained show (Table 2), optimum separation of titanium and vanadium with diethyldithiocarbamate is achieved in the presence of tartaric acid at pH 3-4, and in the presence of ammonium fluoride at pH 5-6. Satisfactory results are obtained in the presence of citric acid at pH 2.5-3. The amount of vanadium in the aqueous phase increases with increasing pH.

Method for Determining Titanium in TiC-V Alloys. A 0.1-0.2 g of alloy is dissolved in a mixture of 20 ml H_2SO_4 (1:4) and 5 ml HNO_3 (sp.gr. 1.43). When dissolution is complete the solution is evaporated to the appearance of thick SO_3 fumes. 25 ml of 1 M tartaric acid solution is added to the cooled solution. By adding ammonia solution dropwise the pH of the solution is adjusted to 3-4; 20 ml of acetate-ammoniacal buffer with pH 3-4 is added. The solution is transferred to a separating funnel and dry sodium diethyldithiocarbamate added in small portions. The yellow-orange colored precipitate of vanadium diethyldithiocarbamate is extracted with chloroform. The pH of the

aqueous layer is checked by universal indicator paper, and, if necessary, 1-2 drops of hydrochloric acid added; precipitation of vanadium with diethyldithiocarbamate is then repeated. After the second precipitation the aqueous layer which is free from vanadium is transferred to a beaker, and boiled until the solution clears; 20 ml of H_2SO_4 (1:1) is added and titanium determined by one of the known methods. 1-2 g of ammonium fluoride can be used instead of tartaric acid; when ammonium fluoride is used the pH should be 5-6. The titanium in the aqueous phase is determined titrimetrically.

TABLE 3.

Sample	C_{total}, %	V, %	Ti found, %			
1*	18,00	4,45	74,40:	75,09	74,85	
2*	18,60	8,20	71,43;	71,35		
3*	16,40	16.50	63,43;	63,04;	63,24;	63,40
4*	15,20	23,0	57,65;	57,57;	57,45	
5*	18,50	42,0	39,50;	39,20		
6*	14,7	30.0	51,90;		51,45	
7*	8,3	57,40	35,02;		34,74	
8*	5,7	64,60	28,94;		29,10	
9*	4,7	74,70	19,16;		19,00	
10*	2,4	88,5	10,0;		10,14	

Vanadium can be determined titrimetrically on a separate aliquot without removal of the titanium, or in the chloroform extract.

Results of analysis of alloys of titanium carbide and vanadium are given in Table 3.

SUMMARY

Conditions for precipitating vanadium with sodium diethyldithiocarbamate in the presence of tartaric, citric, and oxalic acids, and ammonium fluoride have been studied. Complete separation of titanium and vanadium by precipitation with sodium diethyldithiocarbamate is possible in the presence of citric, or tartaric acid or ammonium fluoride at a pH of 2-3, 3-4, and 5-6 respectively.

A method has been developed for the analysis of alloys of titanium carbide and vanadium metal.

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CONDITIONS FOR SEPARATION OF ARSENTIC AND PREPARATION OF THE BLUE ARSENOMOLYBDATE COMPLEX

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Having studied conditions for arsenic determination, Finkel'shtein and Kryuchkova [1] concluded that its determination by distillation of arsenic chloride from a hydrochloric acid solution and absorption with water leads to an appreciable loss of arsenic (from 12 to 40%); these authors recommend therefore that the arsenic chloride be absorbed with a 1% hydrogen peroxide solution. Published information [2-5] indicates that the method outlined for separation of small amounts of arsenic with absorption in water is the best method. We have not observed any loss of arsenic on using this method over a period of several years.

In order to make a comparative study of the absorption of arsenic chloride by water and 1% hydrogen peroxide we carried out a series of experiments on standard samples of agglomerates, cast iron, and steel.

Removal of excess oxidizing agent from the distillate by evaporation to dryness lengthens the determination. Moreover, as published data show, prolonged heating and non-observance of temperature conditions during evaporation to dryness can lead to partial volatilization of arsenic. In this connection, for comparison, we removed excess hydrogen peroxide by evaporation to dryness with nitric acid, and by addition of permanganate solution.

As the results in Table 1 show, positive results were obtained both when arsenic chloride was absorbed with water and with 1% hydrogen peroxide solution. We did not detect any loss in arsenic during its distillation into water, just as we detected no loss previously during numerous experiments.

Finkel'shtein and Kryuchkova explain the loss of arsenic during distillation in water by the fact that the equilibrium $AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$ is shifted to the left as the concentration of the hydrochloric acid which distills over when arsenic chloride increases, while the latter, as a result of these conditions, partially evaporates from the aqueous solution. In the presence of hydrogen peroxide, arsenic acid is formed, and this leads to a shift of the equilibrium to the right.

In order to shift the equilibrium to the right and thereby avoid the possibility of loss of arsenic, we used a solution of ammonia and a solution of sodium hydroxide instead of 1% hydrogen peroxide for absorbing arsenic chloride, the amounts of the respective alkalis taken being sufficient to ensure an alkaline reaction until the end of the distillation of the arsenic.

The results given in Table 1 show that the amounts of arsenic obtained in these cases are again of the same order as when the arsenic chloride is absorbed with water and hydrogen peroxide.

On the basis of Raoult's law and psychrometry we calculated the theoretical possibility of loss of arsenic during its distillation from a hydrochloric acid solution and its absorption with water.

Assuming that all the arsenic is present in the distillate as arsenic chloride and that a small current of carbon dioxide is passed through the solution during distillation, the calculated loss of arsenic amounts to about 0.3%, i.e., it does not, in practice, have any effect on the quantitative determination of arsenic.

Finkel'shtein and Kryuchkova [1] indicate that in the presence of sodium chloride, the stability and reproducibility of the optical density of the solutions deteriorate, while at an appreciable ammonium chloride concentration, the optical density decreases significantly. Since we neutralized the hydrochloric acid distillate with ammonia in the technique we use, it was necessary to check the effect of the salts indicated on the optical density. For this purpose varying amounts of sodium, ammonium, and potassium chlorides, and sodium and potassium sulfates were added to the solution being photometrically measured.

TABLE 1. Absorption of Arsenic Chloride

Arsenic taken for distillation, mg	Arsenic found				
	water	1% H_2O_2 solution		ammonia solution	sodium hydroxide solution
		excess H_2O_2 removed with permanganate	excess H_2O_2 removed by evaporation with HNO_3 to dryness		
0.8	0.79; 0.79	0.81; 0.79	0.81; 0.80	0.80; 0.79	0.81; 0.81
	0.80; 0.81	0.80; 0.81	0.79; 0.80	0.80; 0.80	0.80; 0.82
0.4	0.40; 0.39	0.38; 0.40	0.40; 0.39	0.41; 0.40	0.40; 0.41
	0.39; 0.40	0.41	0.41	0.40	
0.2	0.21; 0.20	0.20; 0.20	0.19; 0.20	0.20; 0.21	0.19; 0.21
	0.20; 0.21	0.19; 0.21	0.19	0.20	
Agglomerate, standard sample No. 211	0.128; 0.126	0.13; 0.128	0.127; 0.13		
0.125% As	0.127; 0.126	0.126	0.129	–	–
Agglomerate, standard sample KBK	0.116; 0.118	0.117; 0.12	0.115; 0.117		
0.113% As	0.117	0.116	0.12	–	–
Cast iron, standard sample No. 64	0.149; 0.152	0.15; 0.152	0.152; 0.154	–	–
0.152% As	0.15				
Steel, standard sample No. 199					
0.117% As	0.115; 0.118	0.116; 0.118	0.119; 0.115	–	–

TABLE 2. Effect of NaCl, NH_4Cl, KCl, and Na_2SO_4 on the Optical Density of Solutions of the Blue Arsenomolybdate Complex

Arsenic taken, mg	Amt. of salt added, g	Arsenic found (mg) in the presence of the salts:				
		NaCl	NH_4Cl	KCl	Na_2SO_4	K_2SO_4
0,05	0,5	0,05; 0,051	0,051; 0,05 0,5			
0,1		0,101; 0,101	0,104; 0,1	0,1; 0,101	—	—
0,05	1,0	0,051; 0,05 0,5	0,05; 0,05			
0,1		0,1; 0,108 0,104; 0,106	0,1; 0,102	0,1; 0,1	0,102; 0,101	0,102; 0,102
0,05	2,0	0,056; 0,068	0,05; 0,051 0,05			
0,1		0,106; 0,106	0,1; 0,101	0,101; 0,1	0,103; 0,101	—
0,05	3,0	0,061; 0,06	0,05; 0,052 0,05			
0,1		0,132; 0,112 0,142	0,101; 0,1	0,1; 0,102	0,102; 0,102	0,101; 0,102
0,05	4,0	0,05; 0,051	0,051; 0,05			
0,1		0,1; 0,098	0,102; 0,101	0,097; 0,098	0,101; 0,102	—
0,05	5,0	0,042; 0,044	0,049; 0,05			
0,1		0,069; 0,067	0,098; 0,097	0,08; 0,081	0,102; 0,102	0,102; 0,102
0,1	7,0	0,022; 0,023	0,096; 0,1	0,036; 0,038	0,101; 0,103	0 101; 0,102
0,1	10,0	No blue color	0,108; 0,11	No blue color	0,102; 0,104	—

The results given in Table 2 show that the reproducibility of the optical density deteriorates in the presence of sodium and potassium chlorides. Starting at a value of 5 g and going upward, the optical density decreases significantly, while in the presence of 10 g of the salts indicated the blue arsenomolybdate complex is not formed at all. Ammonium chloride and sodium sulfate in amounts up to 10 g, and potassium sulfate in amounts up to 7 g, do not affect the optical density.

The different effect shown by the chlorides and sulfates of the alkali metals is explained by the fact that arsenic chloride is capable of forming the compounds $M(AsCl_4)$, $M_2(AsCl_6)$ [6] with the chlorides of the univalent metals.

Finkel'shtein and Kryuchkova recommend that the distillation be carried out without passage of carbon dioxide or nitrogen. Our many years experience has shown that it is much more convenient to pass carbon dioxide through the solution at a rate of 1-2 bubbles per second during distillation. Passage of carbon dioxide promotes volatilization of the arsenic, prevents suck back of the distillate in the condenser, and helps to maintain smooth and uniform boiling. This is particularly convenient when several distillation setups are in simultaneous use.

Finkel'shtein and Kryuchkova indicate that the acidity of the solution being photometrically measured should lie within the limits 0.1-0.5 N. One of the authors of the present article [7] during a study of the effect of acidity and the amount of ammonium molybdate on the color intensity of blue arsenomolybdic acid, established that the amount of ammonium molybdate has an essential influence on the maximum permissible acidity of the solution, the permissible acidity being higher the greater the excess of ammonium molybdate used. Using the amount of molybdate recommended by Finkel'shtein and Kryuchkova in their analytical procedure for arsenic determination, the permissible acidity should lie within the range 0.2-0.35 N; at 0.1 N reduction of excess molybdate will occur, while at 0.4 N and upward, appreciable weakening of the color will be observed.

SUMMARY

The method of distilling arsenic chloride from a hydrochloric acid solution with subsequent absorption in water gives completely reliable results for low arsenic contents.

When arsenic chloride is absorbed with hydrogen peroxide solution, excess of the latter can be removed with permanganate solution, without resorting to evaporation to dryness.

Alkali metal chlorides lead to a deterioration in the stability and reproducibility of the optical density of the solution, while at relatively high contents of these salts the optical density decreases significantly. Ammonium chloride and alkali metal sulfates do not affect the optical density.

Passage of carbon dioxide through the solution during distillation improves the conditions for volatilization of arsenic chloride.

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2,3-DIMERCAPTOPROPIONIC ACID AS A REAGENT FOR MOLYBDENUM

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2,3-Dimercaptopropionic acid $CH_2(SH)-CH(SH)-COOH$ and dimercaptopropanol (BAL) $CH_2(SH)-CH(SH)-CH_2(OH)$ contain a combination of atoms which ensure that they interact with sexi- and quinquevalent molybdenum to form yellow colored compounds [1]. Both compounds permit detection of very small amounts of molybdenum; nevertheless, dimercaptopropanol is less suitable than 2,3-dimercaptopropionic acid for the photometric determination of molybdenum, as our experiments have shown. Accordingly, we only studied 2,3-dimercaptopropionic acid in detail as a reagent for molybdenum.

Dibromopropionic acid was used as starting material for preparation of 2,3-dimercaptopropionic acid [2]. The yield was about 30%.

Experiments showed that sodium molybdate reacts with excess 2,3-dimercaptopropionic acid at acidities ranging from pH 6 to 6 N HCl. A greenish-yellow color appears immediately in weakly acid (pH 3) and strongly acid (0.2 N HCl) media. Under such conditions quinquevalent molybdenum gives a yellow colored compound with the reagent.

The quinquevalent molybdenum compound has a less intense color than that of sexivalent molybdenum (under comparable conditions).

In the presence of a relatively small excess of reagent (e.g., a ten-fold excess in moles) the optical density of solutions of the sexi- and quinquevalent molybdenum compounds formed (about 10^{-4} M Mo^{VI} or Mo^{V}) attains a constant value very slowly at pH 1.3-4 (e.g., after 1 hr 30 min). When the reagent is present in an appreciable excess (e.g., 100-fold and more in moles) the optical density acquires a constant value in 10 min over the acidity range pH 2 to 5 N HCl, and does not change over a period of more than three hours.

After reaching a constant value, the maximum optical density is observed at pH 3.5-5.0 in the case of the sexivalent molybdenum compound, while in the case of the quinquevalent molybdenum compound the maximum optical density is observed at pH 1.4-4.7 (for a ten-fold molar excess of reagent).

Absorption curves of solutions of the compounds of sexivalent and quinquevalent molybdenum with 2,3-dimercaptopropionic acid are shown in Fig. 1. All these curves were obtained using a ten-fold molar excess of reagent. The optical density was measured when it had reached a constant value. The absorption curve of the solution of the sexivalent molybdenum compound has a maximum at 360 mμ after 20 min at pH 4.84 (Fig. 1, curve 1). After 24 hr the same solution has an absorption maximum at 330 mμ (Fig. 1, curve 2). It coincides with the absorption maximum of solutions of the quinquevalent molybdenum compound at pH 1.4 (Fig. 1, curve 4).

The maximum of the absorption curves of solutions of the sexivalent molybdenum compound after 21 hr at pH 1.05 (Curve 3, Fig. 1) and of solutions of the quinquevalent molybdenum compound 10 min after preparation at pH 1.4 (Fig. 1, curve 4) also coincide.

Solutions of 2,3-dimercaptopropionic acid hardly absorb any light at 360 mμ and 330 mμ.

The absorption maximum and the apparent molar extinction coefficient of solutions of the compounds formed on mixing solutions of quinquevalent and sexivalent molybdenum with 2,3-dimercaptopropionic acid at pH 1 and in

a 3 N HCl medium almost coincide with each other (Table 1). This gives grounds for assuming that at pH 1 and in a 3 N HCl medium, excess of reagent reduces sexivalent molybdenum to the quinquevalent state, forming a colored compound with it. The reduction rate is strongly dependent on the acidity of the solution.

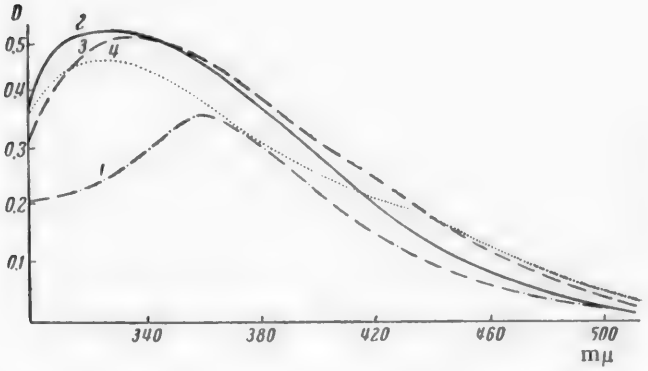


Fig. 1. Absorption curves of solutions of the compounds of sexivalent and quinquevalent molybdenum with 2,3-dimercaptopropionic acid. The concentration of Mo^{VI} and Mo^{V} was the same in all the solutions and equal to 1.03×10^{-4} M; the reagent concentration was 10^{-3}M. 1) Mo^{VI}, pH 4.84, 10 min after preparation of the solution; 2) Mo^{VI}, pH 4.84, 28 hr after preparation of the solution; 3) Mo^{VI}, pH 1.05, 21 hr after preparation of the solution; 4) Mo^{V}, pH 1.4, 10 min after preparation of the solution.

The molar ratios which obtain during the interaction of sexivalent and quinquevalent molybdenum with 2,3-dimercaptopropionic acid were established by the isomolar series method. Different volumes of a 0.01069 M solution of sodium molybdate or of a quinquevalent molybdenum salt (the latter in 1 N HCl) were mixed with a neutral 0.01089 M solution of 2,3-dimercaptopropionic acid so that the sum of the molar concentrations of both components in the final volume was constant and equal to 8.71×10^{-4}M.

The 2,3-dimercaptopropionic acid concentration in the original solution was determined by potentiometric titration with 0.01 N NaOH.

Experiments were carried out at pH 0.92 and 4.84 (Figs. 2, 3) in the case of sexivalent molybdenum. Buffer solutions with pH 0.92 and 3.84 were used for adjusting the pH to the required value.

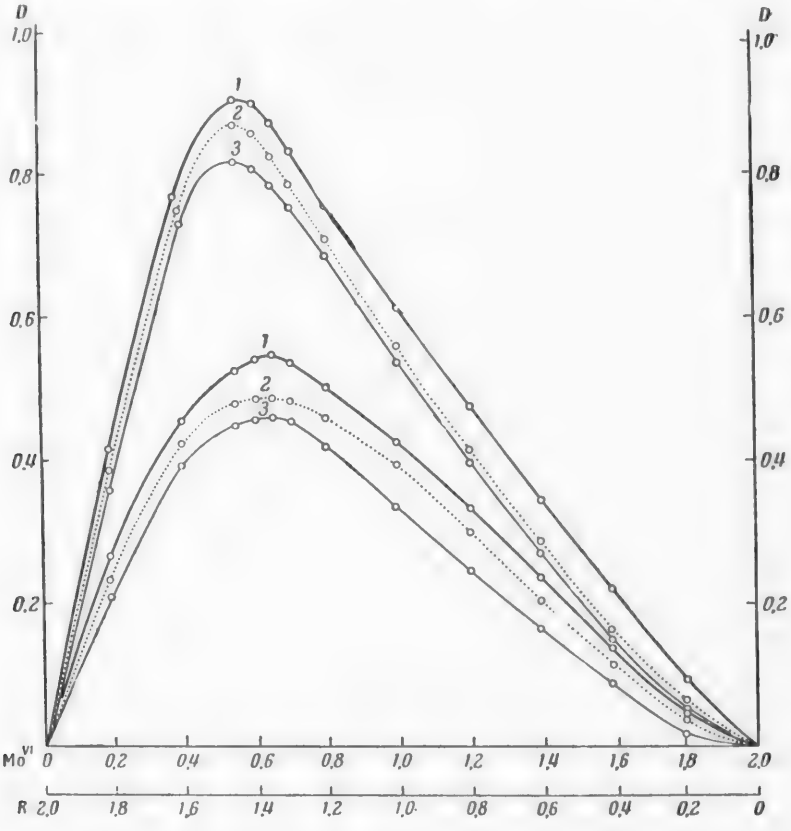


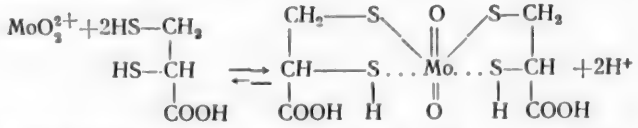
Fig. 2. Molar ratio during interaction of sexivalent molybdenum with 2,3-dimercaptopropionic acid (pH 0.92). 1) At 329 mμ; 2) at 350 mμ; 3) at 358 mμ. The optical density was measured 20 min, 3 hr, and 24 hr after preparation of the solutions.

The optical density was measured at 329, 350, and 358 mμ, 10 min, 3 hr, and 24 hr after preparation of the solutions. Experiments with quinquevalent molybdenum were carried out at pH 0.92 (Fig.4).

TABLE 1. The Final Molybdenum Concentration was 1.03×10^{-4}M

Valence of molybdenum	D (l = 1 cm)		ε		Acidity
	329 mμ	360 mμ	329 mμ	360 mμ	
Mo^{V}	0.430	0.435	4200	4200	3 M
	0.450	0.460	4400	4400	3 M
Mo^{VI}	0.460	0.460	4400	4400	pH 1

At pH 0.92 sexivalent molybdenum initially reacts with 2,3-dimercaptopropionic acid at a molar ratio of 1:2, probably according to the following equation:



After 24 hr the molar ratios altered (at pH 4.84) and proved to be 2:5. This result can be explained by assuming that sexivalent molybdenum is reduced to the quinquevalent state (one mole of 2,3-dimercaptopropionic acid is expended on two moles of sexivalent molybdenum), and that subsequently two moles of quinquevalent molybdenum react with four moles of 2,3-dimercaptopropionic acid to give a compound at a ratio of 1:2. The molar ratios determined by measuring the optical density three hours after preparing the solutions at pH 4.84 proved to be intermediate between 1:2 and 2:5 (Fig. 3).

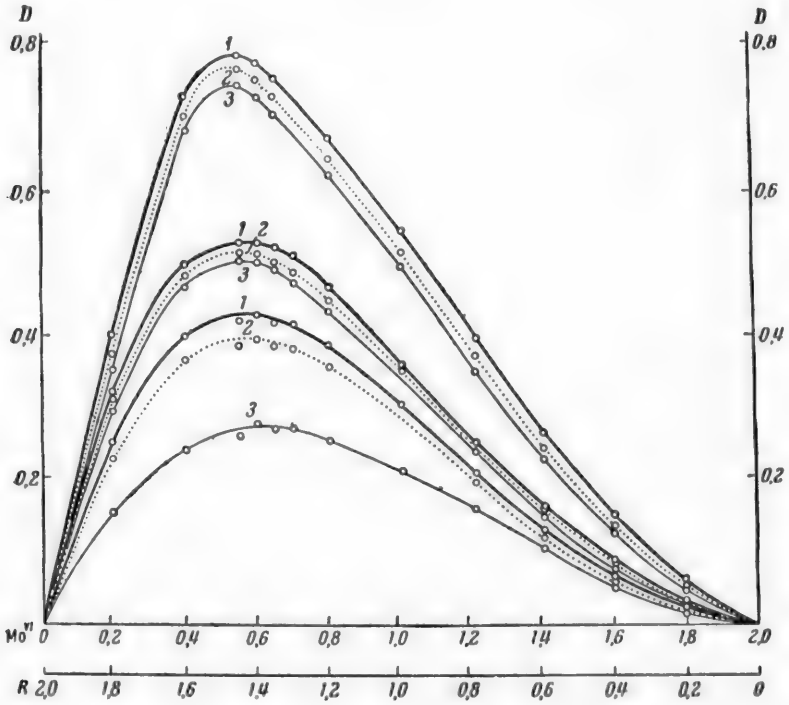


Fig. 3. Molar ratios during interaction of sexivalent molybdenum with 2,3-dimercaptopropionic acid (pH 4.84). 1) At 329 mμ; 2) at 350 mμ; 3) at 358 mμ. The optical density was measured 10 min, 3 hr, and 24 hr after the solutions had been prepared.

The maximum optical density in experiments with quinquevalent molybdenum was found at a molar ratio of molybdenum to 2,3-dimercaptopropionic acid of 1:2 (Fig. 4). The reaction, presumably, proceeds according to the equation:

$$Mo_2O_3^{4+} + 4CH_2(SH) - CH(SH) - COOH \rightleftharpoons Mo_2O_3[S - CH_2 - CH(SH) - COOH]_4 + 4H^+$$

The possibility of determining molybdenum photometrically was studied in a medium of 3 N HCl and 0.2 N HCl, using a large excess of 2,3-dimercaptopropionic acid, which, at such an acidity completely and rapidly reduces molybdenum to the quinquevalent state and then forms a sufficiently intensely yellow colored compound. Over the acidity ranges pH 2 to 1.0 N HCl, and 1.5 N to 5 N HCl, the optical density of the solutions obtained hardly changes at all. At a final concentration of 2,3-dimercaptopropionic acid of 10^{-2}M, the optical density of 10^{-4}M solutions of molybdenum reaches a maximum value in 3 hr, and this value remains almost constant on increasing the reagent concentration further.

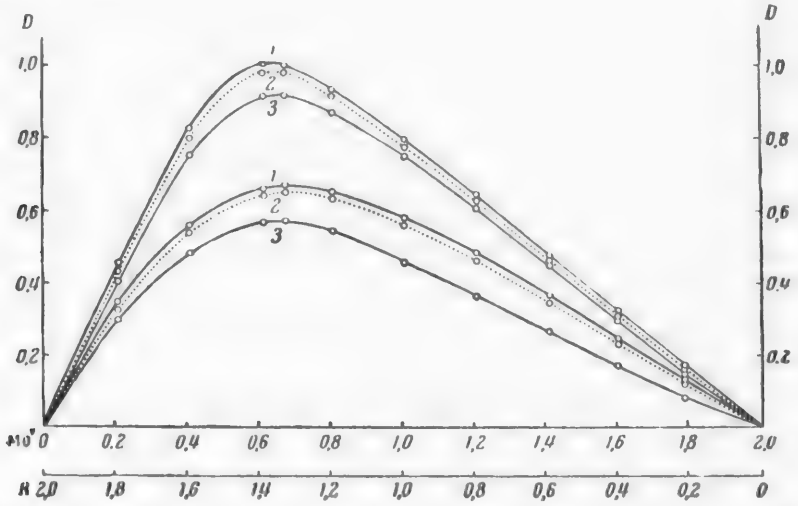


Fig. 4. Molar ratios during interaction of quinquevalent with 2,3-dimercaptopropionic acid (pH 0.96). 1) At 329 mμ; 2) at 340 mμ; 3) at 358 mμ. The optical density was measured 10 min, and 24 hr after the solutions had been prepared.

A calibration curve was constructed as follows: 5 to 0.5 ml aliquots of 2.5×10^{-3}M sodium molybdate solution were introduced into 25 ml flasks, and 6.5 ml of concentrated hydrochloric acid and 3.75 ml of 0.1 M 2,3-dimercaptopropionic acid (150-fold excess with respect to molybdenum) added to each, the volumes of the solutions were made up to the mark with water and the flasks shaken. The hydrochloric acid concentration of the final solution was about 3 N.

The optical density was measured after 10 min with respect to water in a cell with a path length of 1 cm, using a SF-4 spectrophotometer at 329 mμ or at 350 mμ. The solutions conform well to Beer's law over the range 2.5 μg Mo/ml to 39.4 μg Mo/ml.

Molybdenum was determined photometrically under the same conditions as those used for constructing the calibration curve.

Copper ions give a dark-blue precipitate with the reagent and interfere with molybdenum determination. Thiourea cannot be used for masking copper since nonreproducible and incorrect results are obtained. Divalent iron does not interfere with molybdenum determination; trivalent iron gives a dark-blue color which disappears on adding excess reagent. Divalent mercury forms a white, clotted precipitate with the reagent.

Lead, chromium, aluminum, nickel, cobalt, zirconium, titanium, tungsten, zinc, manganese, and barium ions do not give a color or precipitate with the reagent. Nevertheless, molybdenum cannot be determined in the presence of these elements, since a white turbidity appears, the amount of which increases with time.

We also studied the possibility of determining molybdenum in the presence of foreign elements in a medium of 0.2 N HCl. The calibration curve was constructed as in the previous case. These solutions also conformed well to Beer's law over the range 4 μg/ml to 40 μg/ml. Water was used as the reference solution (Fig. 5).

Satisfactory results were obtained in the presence of large amounts of zirconium, titanium, chromium, cobalt, nickel, aluminum, zinc, and manganese (Table 2). In the presence of chromium the optical density should be measured immediately, since after two hours high results are obtained. Tungsten is precipitated as tungstic acid; after filtering off the latter low results are obtained for molybdenum. Lead is precipitated as its chloride. When bismuth is present a turbidity appears. Divalent copper and univalent mercury interfere. Trivalent iron should be reduced to the divalent state with ascorbic acid.

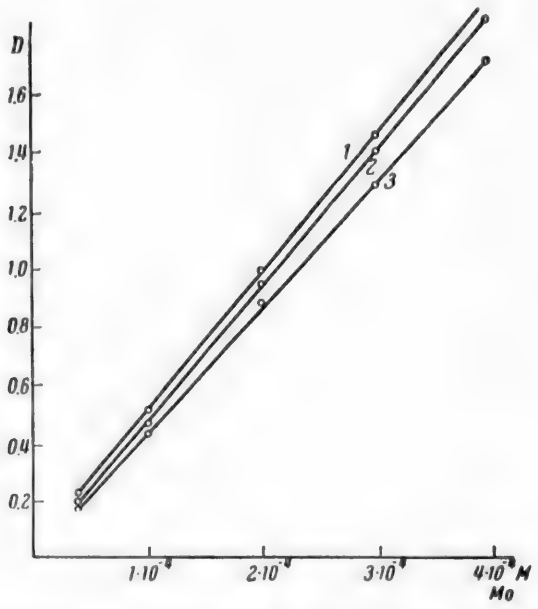


Fig. 5. Conformation of solutions of the compounds of molybdenum with 2,3-dimercaptopropionic acid in 0.2 N HCl to Beer's law; Mo:R = 1:150. 1) 330 mμ; 2) 360 mμ; 3) 380 mμ.

TABLE 2. (0.24 mg Mo taken; final acid concentration 0.2 N HCl)

Foreign elements, mg	Mo found, mg	Error, mg	Foreign elements, mg	Mo found, mg	Error, mg
10 Zn	0,24	0,00	10W**	0,21	—0,03
5 Ti	0,24	0,00	20Zn	0,24	0,00
20 Cr°°	0,24	0,00	20Mn	0,24	0,00
2 Bi	0,47	+0,23	40Fe⁺²***	0,26	+0,02
40 Ni	0,24	0,00	40Fe⁺³****	0,26	+0,02
20 Co	0,23	—0,01	40Fe⁺³°	0,47	+0,23
20Pb*	0,19	—0,05	20Al	0,23	—0,01

* After filtering off the $PbCl_2$ precipitate.

** After filtering off the turbidity from tungstic acid.

*** In the presence of 0.77 g ascorbic acid.

**** In the presence of 1.13 g ascorbic acid.

° In the presence of 0.25 ml of concentrated H_3PO_4.

°° Results were high by 0.02 mg after 2 hr.

SUMMARY

The interaction of 2,3-dimercaptopropionic acid with sexi- and quinquevalent molybdenum has been studied. It has been shown that molybdenum can be determined photometrically in the presence of a number of elements.

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A STUDY OF THE INTERACTION OF MOLYBDENUM WITH 8-MERCAPTOQUINOLINE

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A number of papers devoted to the analytical application of 8-mercaptoquinoline have been published recently [1-4]. The composition, as determined by chemical analysis, of the compounds formed between 8-mercapotquinoline and various cations [4,5] cannot completely characterize the processes which occur in solution. The work described here is devoted to a study of the interaction of sexivalent molybdenum and 8-mercaptoquinoline (thiooxine) in solution, and to the determination of the composition and stability of the compound formed.

EXPERIMENTAL

Measurements were carried out on a FEK-M colorimeter and on a PPTV-1 potentiometer. Solutions were prepared by dissolving the recrystallized salts in twice distilled water.

Potentiometric Method. Thiooxine hydrochloride possesses reducing properties. In order to establish the amount of thiooxine which is sufficient for reducing sexivalent molybdenum, the change in the emf of the system Mo^{VI}/Mo^{x} during titration of a hydrochloric acid solution of molybdate (3 N) was established. A concentration circuit was set up in which a platinum electrode in a molybdate solution (Mo^{VI}) served as anode, while the cathode was a platinum electrode in a molybdate (Mo^{VI}) solution which was being titrated with an equimolar thiooxine solution. Completion of reduction was determined on the basis of a sharp change in potential.

As Fig. 1 shows the maximum emf change was observed on adding one mole of thioxine to one mole of molybdate. Thus sexivalent molybdenum is reduced by thiooxine to lower oxidation states.

We used an optical method for determining the stoichiometric coefficients of the reaction between molybdate and thiooxine in toluene.

Optical Method. When neither the composition of the compound formed or its state in solution are known, it is possible, using the method of limiting logarithms, to establish the number of coordinated groups in the compound.

We represent the reaction which we are interested in as follows:

$$n\,MoO_xZ^y + m\,[C_9H_6NS]^- \rightleftarrows (MoO_xZ^y)_n\,(C_9H_6NS)_m \qquad (1)$$

where MoO_xZ_y is the ion containing the reduced molybdenum. The equilibrium constant of this reaction is equal to:

$$K = \frac{[A]^n\,[B]^m}{[A_nB_m]}, \qquad (2)$$

where A is $[A]-[MoO_xZ^y]$, and [B] is $[B]-[C_9H_6NS]$. In logarithmic form: $\log K = n \log [A] + m \log [A_nB_m]$,

or
$$\lg [A_nB_m] = n \lg [A] + m \lg [B] - \lg K. \qquad (3)$$

When the concentration of one of the components, e.g., [A], is constant while the concentration of [B] alters, then $\log [A_nB_m]$ will be a linear function of log [B].

If the optical density D is used as a characteristic of the change in concentration $[A_nB_m]$, then log D should be a linear function of log [B].

On constructing the curve log D−log [B] we obtain a straight line, the tangent of the slope of which gives the value of n. m can be determined in exactly the same way.

The concentration of one of the components of the reaction was kept constant while that of the other component was varied, and the optimum ratio of the reactants determined.

A series of experiments was carried out with solutions of sexivalent molybdenum. The procedure adopted was as follows: concentrated hydrochloric acid was added to a molybdate (VI) solution (until the normality of the final solution was 2.56-3.50); this was followed by thiooxine solution and toluene. The mixture was shaken for 5 min. The organic layer was then removed and its optical density measured at 420 mμ.

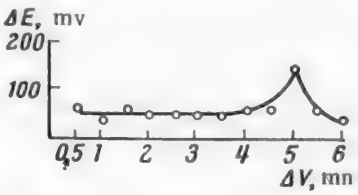

Fig. 1. Potentiometric titration of 5.0 ml of 0.00058 M molybdenum solution with 0.00058 M thiooxine solution.

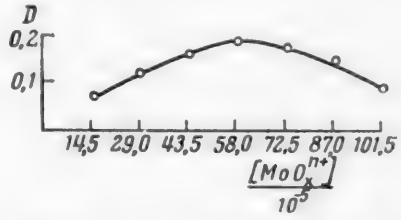

Fig. 2. Change in optical density with change in thiooxine concentration when the molybdenum (VI) concentration is kept constant.

The change in optical density with changes in molybdenum (VI) concentration (while the thiooxine concentration is constant) was found to have a maximum value at a ratio of 1:1, as Fig. 2 shows. In the experiments where this ratio was high, the optical density fell.

This fact shows that the colored compound is formed, apparently, between the reduced molybdenum and the residue of unoxidized thiooxine.

We assumed that reduction of sexivalent molybdenum by thiooxine proceeded to the quinquevalent state. This assumption is supported by the fact that Mo^{V} obtained by reduction with mercury metal in hydrochloric acid solution (3N) [10], gave an exactly similar colored compound with thiooxine as Mo^{VI}. The maximum absorption of this compound was also found to occur at 420 mμ.

In addition, a study of the optical density at a constant thiooxine concentration and varying Mo^{V} concentrations showed (Fig. 3) that the optical density remains constant after the maximum value has been reached. Changes in optical density with changes in molybdenum concentration for a constant thiooxine concentration are given in Table 1.

TABLE 1. Relation between Optical Density and Molybdenum Concentration (At a constant thiooxine concentration of 0.0378 g.ion liter)

Mo^{V} concentration, M	-log[MoO_xZ_y]	D	-log D	n	Mo^{V} concentration, M	-log[MoO_xZ_y]	D	-log D	m
$58 \cdot 10^{-7}$	5.24	0.025	1.61		$69.6 \cdot 10^{-6}$	4.17	0.120	0.92	
$11.6 \cdot 10^{-6}$	4.93	0.057	1.25		$92.8 \cdot 10^{-6}$	4.03	0.145	0.75	
$23.2 \cdot 10^{-6}$	4.64	0.085	1.07		$11.6 \cdot 10^{-5}$	3.93	0.120	0.92	
$46.4 \cdot 10^{-6}$	4.39	0.100	1.00	1.93					

The changes in optical density with changes in thiooxine concentration while the Mo^{V} concentration is constant are given in Table 2.

As Tables 1 and 2, and Figs. 3 and 4, show, the coefficients n and m in equation 1 are equal to 2.

Radiometric Method. We decided it would be expedient to calculate $K_{instab.}$ of the compound obtained in toluene by a radiometric method, by establishing the partition coefficient of molybdenum thiooxinate between the organic and aqueous phases.

Molybdenum thiooxinate was prepared under the optimum reaction conditions [4,5]. Having determined the concentration of molybdenum in the aqueous phase, we established the equilibrium concentration of molybdenum

not entering into a compound with thiooxine. Having determined the molybdenum concentration of the organic phase, we established the concentration of the compound of molybdenum with thiooxine.

The experimental procedure was as follows. Water was added to solutions containing different amounts of Mo^{99} so that the total volume in each case was 5 ml, 1.5 ml of concentrated HC-; 0.38 ml of thiooxine (5% solution), and 1.5 ml of toluene were then added and the mixtures shaken for 3 min. The organic and aqueous phases were removed from each other and evaporated separately; the activity of the dry residues was then measured on a counter of the VSP-1957-2753 type.

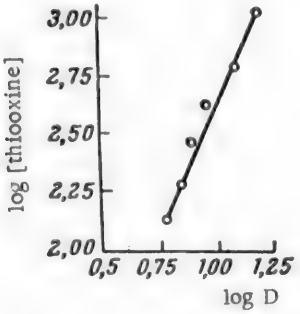

Fig. 3. Relation between log optical density and log thiooxine concentration.

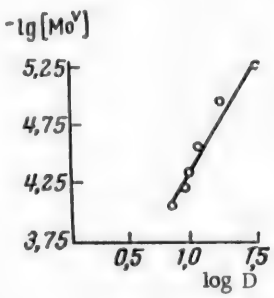

Fig. 4. Relation between log optical density and log Mo^V concentration.

The molybdenum concentration can be estimated from the calibration curve constructed within the coordinates Mo^{99} concentration–activity (cpm). The background was calculated before each determination.

A standard solution of $(NH_4)_2MoO_4$ prepared from an aliquot of active MoO_3 was used for constructing the calibration curve.

The value of arbitrary $K_{instab.}$ calculated by means of equation 2 (using mean values) was 7.80×10^{-4}.

The partition of molybdenum was studied in solutions whose acidity with respect to HCl was 1.15, 2.18, and 3.25 N. Under these conditions the stability of the compound proved to be the same.

TABLE 2. Relation between Optical Density and Thiooxine Concentration (At a Mo^V concentration of 0.000058 g.ion liter)

Thiooxine concentration, M	-log [thiooxine]	D	-log D	m	Thiooxine concentration μg/ml	-log [thiooxine]	D	-log D	m
$8.56 \cdot 10^{-4}$	3.07	0.075	1.15		$34.24 \cdot 10^{-4}$	2.46	0.135	0.87	
$17.12 \cdot 10^{-4}$	2.76	0.080	1.10		$51.36 \cdot 10^{-4}$	2.28	0.138	0.86	
$25.68 \cdot 10^{-4}$	2.69	0.125	0.90	2	$68.48 \cdot 10^{-4}$	2.16	0.140	0.76	

TABLE 3. Determination of $K_{instab.}$ by a Radiometric Method

Molybdenum concentration, μg/ml	No. of impulses, cpm		Equilibrium concentration of molybdenum, g. ion/liter	Excess thiooxine concentration, g. ion/liter	Concentration of the complex g. ion/liter
	aqueous phase	organic phase			
1.5	100				
3.0	203				
6.0	426				
3.0	18	180	0.155	0.0140	2.70
3.0	12	170	0.230	0.0137	2.40
3.6	34	230	0.400	0.0105	3.30
3.6	40	240	0.150	0.0145	3.60
3.0	5	105	0.080	0.0153	2.85
3.0	7	180	0.100	0.0155	2.55

Composition of the Compound Formed between Molybdenum and Thiooxine. Having established the stoichiometric coefficients of the compound of molybdenum with thiooxine, and the stability of the compound formed, we decided to attempt to establish the formula of this compound. For this purpose it was necessary to establish the valence of molybdenum in the compound.

Published information on the valence of molybdenum in this compound is contradictory.

Bankovskii in one of his earlier papers [5] gives the following formulas for compounds of molybdenum with thiooxine in a weakly acid medium (pH 2÷3): $Mo_2O_3(C_9H_6NS)_2 \cdot H_2O$ – a compound with a green color.

In the presence of strong reducing agents ($TiCl_3$, $SnCl_2$) the yellow colored compound $MoO(C_9H_6NS) \cdot {}^1/_2H_2O$ – is formed.

The valence of molybdenum in the first compound is, presumably, four while in the second it is three. In more recent papers Bankovskii gives the following formula for the compound of molybdenum with thiooxine: $MoO_2(C_9H_6NS)_2 \cdot H_2O$. The valence of molybdenum in this compound is obviously six. Such a compound is formed at pH 2-3 and lower [4].

Bankovskii established the composition of the thiooxinates by a preparative method.

We [6], like Bankovskii, have pointed out that thiooxinates of different colors are formed depending on the acidity. In weakly acid media orange-green colored thiooxinates are formed, while in more acid media yellow to brown-reddish thiooxinates are formed. Nevertheless we are not inclined to explain the difference in color of the thiooxinates formed by differences in the degree to which molybdenum is reduced, but consider it more likely that it is determined by differences in the state of the molybdenum as a function of the degree of acidity.

According to published information, and according to our studies [7, 8], molybdenum forms complex compounds which are anionic in character when the acid concentration exceeds 1.0 N (with respect to HCl), while over the acidity range 0.1-1 N molybdenum is found in the form of MoO_2^{2+}.

Chloride complexes of quinquevalent molybdenum are described in a paper by Babko and Get'man [9]. The authors also point out changes in color of solutions containing molybdenum with changes in HCl concentration, and, on the basis of the character of the spectrophotometric curves, state that Cl^- does not simply enter into the inner coordination sphere of the complex, but expels oxygen ions. Babko and Get'man also put forward the suggestion that quinquevalent molybdenum exists in the form MoO_2^+ up to a HCl concentration of 2 N. On increasing the HCl concentration above 3 N, MoO^{3+} will dominate. The MoO^{3+} is capable of reacting with Cl^- even in dilute solutions with formation of unstable and colorless complexes of $MoOCl_2^+$ and $MoOCl^{2+}$, while in the presence of a large excess of Cl^- the colored complex $MoOCl_3$ is formed.

These results are in good agreement with the ones we obtained by a kinetic method for Mo^{VI} [7]. Total $K_{instab.} = 5 \times 10^{-3}$ for $MoOCl_3$ [9].

K for the first dissociation stage, obviously, has a large value. It is possible that the reaction with thiooxine proceeds as follows in the aqueous phase:

$$n\,MoOCl_3 + m\,K(C_9H_6NS) = \underline{[MoOCl_2]_n\,[C_9H_6NS]_m} + KCl.$$

The very low solubility of molybdenum thiooxinate (precipitates are formed even in 4.0 N HCl) [6,4] supports this assumption.

It is probable that the differences in the color of molybdenum thiooxinates is determined by differences in the composition of the chloride complex ions which interact with thiooxine.

During a check on the effect of reducing agents on the nature of the interaction of molybdenum with thiooxine, it was found that ascorbic acid present in a sample does not alter the optical density of the compound formed with thiooxine as compared with the optical density of the compound obtained in the absence of any foreign reducing agents. It is obvious that thiooxine itself reduced Mo^{VI} to Mo^V. We assumed the following mechanism for the reaction: Mo^{VI} is reduced by thiooxine in a hydrochloric acid medium to Mo^V, and the latter in the form of a chloride complex cation reacts with excess thiooxine.

The results obtained by the preparative method published by Bankovskii support this assumption. In a strongly acid medium (HCl 1:1) he obtained a compound containing 16.4% Mo, 18.14% Cl, and 4.95% N; in a weakly acid medium (pH 2-3 and in more acid regions) the compound obtained 20.64% Mo, 6.29% N, and 13.67% S.

Thus on the basis of what has been said above it can be assumed that the compound of molybdenum with thiooxine in a medium of 2.5-3.0 N HCl has the formula: $(MoOCl_2)_2(C_9H_6NS)_2$. In a weakly acid medium (up to 1 N HCl) the compound $(MoO_2)_2(C_9H_6NS)_2$ is formed.

SUMMARY

The stoichiometric coefficients of the reaction between molybdenum and thiooxine have been determined by optical and potentiometric methods. The partition coefficient of molybdenum thiooxinate has been determined, and $K_{instab.}$ of the compound formed in toluene established.

The value of $K_{instab.}$ does not depend on the acidity over the acidity range studied, 1.15 N to 3.25 N HCl.

The value of $K_{instab.}$ was found to be 7.8×10^{-4}.

On the basis of published information and of the authors' own research work it is suggested that the compounds formed between molybdenum and thiooxine have the following compositions: in a weakly acid medium $(MoOCl_2)_2(C_9H_6NS)_2$ and in a strongly acid medium $(MoO_2)_2(C_9H_6NS)_2$.

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AMPEROMETRIC TITRATION OF VANDIUM AND URANIUM WITH TRIVALENT TITANIUM SALTS

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The use of compounds of certain elements in their lower valence states as reagents permits determination of elements in complex mixtures in certain cases. The use of trivalent titanium salts for the determination of some oxidizing agents in the presence of appreciable amounts of quadrivalent titanium would appear to hold promise. Solutions of trivalent titanium salts have been used in visual methods of volumetric analysis for the determination of iron [1], iodates [2] and chlorates [3], while they have been used in potentiometric methods for the determination of copper, mercury, bismuth, gold, ruthenium, osmium, molybdenum, and selenium.

Trivalent titanium compounds have not been used as reagents in amperometric titration. We established earlier [4] that titanium is oxidized on a rotating platinum microelectrode, and that at a potential of 0.4-0.9 v, the diffusion current is proportional to titanium concentration. This valuable property of trivalent titanium salts can be used for the amperometric titration of a number of oxidizing agents using anodic polarization of a platinum microelectrode. Since trivalent titanium is a fairly strong reducing agent ($E_0 Ti_{IV}/Ti_{II} = -0.04$ v), we thought it would be interesting to use it as a titrant for determining sexivalent uranium ($E_0 UO_2^{2+}/U^{IV} = +0.407$ v) and vanadium in its quadri- and quinquevalent states, in pure salts and in the presence of quadrivalent titanium.

All the work was carried out on a visual type polarograph (Geologopribor) fitted with a M-21 galvanometer (maximum sensitivity 2.4×10^{-9} amp/mm/m). The indicator electrode was the usual type of rotating platinum microelectrode (5 mm long) while the reference electrode was a saturated calomel half-element. The solution was prepared by appropriate dilution of 15% commercial $TiCl_3$ solution with acids (either HCl 1:1 or 4 N H_2SO_4). The solutions were stored in dark glass bottles [5]. Since trivalent titanium compounds are readily oxidized in air, the reagent was stored under purified nitrogen and all experiments were carried out under purified nitrogen. The concentration of the working solution was checked potentiometrically or amperometrically against standard potassium dichromate [4]. The solution was stable for three weeks.

Titration of Quinque- and Quadrivalent Vanadium. Depending on the conditions, quinquevalent vanadium compounds are reduced by trivalent titanium to the quadri- or trivalent state (in the latter case reduction does not always proceed quantitatively).

Quinquevalent vanadium is quantitatively reduced to the trivalent state in a supporting electrolyte of H_2SO_4 starting at a concentration of 0.5 N. In a supporting electrolyte of 0.1 M sodium tartrate (pH 5.9) vanadium is only reduced to the quadrivalent state. In a supporting electrolyte of hydrochloric acid of different concentrations quinquevalent vanadium is reduced in a different way from that in which it is reduced in sulfuric acid, because of the formation of chloride complexes of quadrivalent vanadium [6]. Reduction proceeds to the quadrivalent state (the error is, however, 6%).

We thought it would be interesting to study the reduction of V^{IV} with trivalent titanium. All the experiments were carried out with $VOSO_4$ which was prepared by reducing a standard solution of ammonium vandate with sulfur dioxide. Titration was carried out at a potential of 0.8 v using the oxidation current of titanium. The reaction between the materials indicated was studied amperometrically in various supporting electrolytes. As a result the following facts emerged: reduction does not occur in a supporting electrolyte of hydrochloric acid or in 0.1 M sodium tartrate (pH 5.9), while in a sulfuric acid supporting electrolyte V^{IV} is reduced to V^{III}, the reduction going furthest in 10 N H_2SO_4. In the latter instance the error in determining 0.7-0.9 mg V does not exceed 2%.

From the results obtained (Table 1) it follows that solutions of trivalent titanium can be used for amperometric

titration of quadrivalent vanadium, not only in pure salts, but in the presence of appreciable amounts of Cr^{III}, Mn^{II}, and Ti^{IV} in a supporting electrolyte of 10 N H_2SO_4.

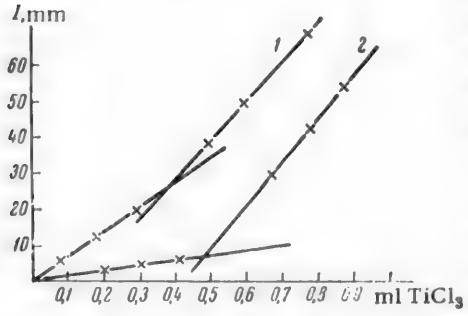
TABLE 1. Determination of Vanadium in a Supporting Electrolyte of 10 N H_2SO_4 in the Presence of Foreign Elements

Foreign elements	V, mg taken	V, mg found	Error, %	Foreign elements	V, mg taken	V, mg found	Error, %
—	0,46	0,45	—2,0	—100	0,68	0,63	—7,0
—	1,39	1,38	—0,7	Ti^{IV} 60	2,00	2,06	3,0
Cr^{3+} 10	0,92	0,91	—1,0	— 60	1,00	1,02	2,0
—100	0,92	0,89	—3,0	—104	1,00	1,04	4,0
Mn^{2+} 50	0,68	0,67	—1,4				

Titration of Sexivalent Uranium. The majority of titrimetric methods of determining uranium are based on its reduction to the quadrivalent state with subsequent titration by some strong oxidizing agent. Earlier, we developed an amperometric method for titrating sexivalent uranium with divalent chromiun salts [7]. This method, however, is only applicable in the presence of approximately equal amounts of uranium (VI) and titanium (IV).

For our work we prepared a solution of uranyl nitrate in sulfuric acid; it was standardized by the ammonia method (5.037 mg U in 1 ml).

Quadrivalent uranium compounds are oxidized under conditions of anodic polarization of a platinum electrode; in a supporting electrolyte of 1 N H_2SO_4 oxidation starts at a potential of approximately 0.5 v. This essentially affects the shape of the titration curve (diagram, curve 1). At room temperature in a supporting electrolyte of sulfuric acid (1-10 N) and hydrochloric acid (1-8 N), titration results are always low, and the error for uranium is very high. Experimental results improve on taking the galvanometer readings three minutes after each addition of reagent (supporting electrolyte 10 N H_2SO_4, curve 2). This, however, appreciably lengthens the time taken for titration. At a solution temperature of about 70° readings can be made after 30 sec. All this indicates that sexivalent uranium is reduced slowly by trivalent titanium.



Titration of quadrivalent uranium with $TiCl_3$ solution in a supporting electrolyte of 10 N H_2SO_4. 1) Galvanometer readings taken after 1 min; 2) readings taken after 3 min.

We studied the effect of traces of Fe^{2+}, Cu^{2+}, and Sn^{2+} on speeding up the reaction. It was found that addition of small amounts of $SnCl_2$ (one drop of a 1% solution) to 10 ml of test solution appreciably speeds up the reaction. This means that uranium can be titrated more quickly, while the experimental error in determining 3-6 mg uranium does not exceed 1%. Pyrophosphoric acid proved even more effective. E. P. Nikolaeva and Yu. M. Shchekochikhin established that addition of pyrophosphoric acid increases $E_{U^{VI}/U^{IV}}$ from 0.4 to 0.6 v. Moreover, it is known that pyrophosphoric acid gives a complex compound with quadrivalent titanium, which, in turn, lowers the redox potential of the system Ti^{IV}/Ti^{III}.

Thus the introduction of this reagent essentially increases the difference in potentials of the reactants. It was established that introduction of pyrophosphoric acid (0.2-0.3 ml of 50% $H_4P_2O_7$) to a supporting electrolyte of 1 N H_2SO_4 permits titration at E = 0.8 v, and, since quadrivalent uranium is not oxidized in the presence of $H_4P_2O_7$, the titration curve has a sharper break. Titration can be carried out taking the galvanometer readings after 30 sec. The error in determining 3-10 mg of uranium does not exceed 1.3%.

Solutions of trivalent titanium permit determination of uranium in the presence of appreciable amounts of quadrivalent titanium (Table 2) when the solution being titrated contains pyrophosphoric acid. Titration in a supporting electrolyte of 1 N H_2SO_4 to which $H_4P_2O_7$ has been added permitted uranium to be determined in the presence of 100 times its amount of titanium, the galvanometer readings being taken 30 sec after addition of titrant.

TABLE 2. Titration of Sexivalent Uranium in the Presence of Quadrivalent Titanium in a Supporting Electrolyte of 1 N H_2SO_4 + $H_4P_2O_7$ (1 ml of 50% $H_4P_2O_7$ in 10 ml solution)

Ti introduced, mg	U, mg		Error, %	Ti introduced, mg	U, mg		Error, %
	Taken	Found			Taken	Found	
—	3,02	3,01	0,3	50	5,04	5,07	0,7
—	5,04	4,96	1,3	15	3,02	3,05	1,0
—	10,08	10,05	0,5	300	3,02	3,08	2,6
5	5,04	5,01	0,5				

SUMMARY

An amperometric method has been developed for titrating quadrivalent vanadium with trivalent titanium in pure salts and in the presence of chromium, manganese, and titanium. Conditions have been established for amperometric titration of uranium with trivalent titanium in the presence of quadrivalent titanium up to a ratio of U:Ti = 1:100.

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QUANTITATIVE DETERMINATION OF URANIUM IN ORES BY AN OSCILLOGRAPHIC POLAROGRAPHIC METHOD

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Several papers have been devoted to the polarographic determination of uranium [1-12]. Nevertheless, many of the published methods involve separation of uranium from a number of accompanying elements and do not satisfy practical requirements.

In order to establish the possibility of determining uranium in ores without separating it from accompanying elements, we used oscillographic polarography. Different methods are used for bringing the ore into solution, depending on the content of uranium, silica, and accompanying elements in the ore. Most uranium ores decomposed with nitric acid to which hydrochloric acid is added in some cases. Ores containing appreciable amounts of silica are treated with a mixture of hydrofluoric and hydrochloric acids [13]. Carbonate ores are decomposed with a mixture of HF and H_2SO_4 or with a mixture of HF and HNO_3. Titanium-niobium ores are fused with a large amount of $K_2S_2O_7$ and the melt dissolved in phosphoric acid. The composition of the supporting electrolyte for polarographing uranium depends on the method used for decomposing the ore.

The reduction and oxidation mechanisms of the products formed during electrolysis of uranyl ions in various media have been studied in fair detail [14-17].

Measurements were made on a GEOKhI Mark 2M oscillographic polarograph [18]. The cell consisted of a dropping mercury electrode and a saturated calomel electrode. The mercury was carefully purified and distilled twice in vacuo. The peak potentials φ_p on the oscillograms were found by a method described earlier [19]; their values are given relative to the saturated calomel electrode (sce). The potential of the dropping electrode (φ) was determined by including a second auxiliary electrode (sce) in the circuit, while the instantaneous potential difference $\varphi_{cathode} - \varphi_{auxiliary}$ was measured by means of a setup specially constructed for measurement of equilibrium emf's [20]. In acid solutions dissolved oxygen does not affect the maximum current of UO_2^{2+}; accordingly uranium was determined quantitatively without removal of oxygen.

Standard solutions were prepared by dissolving chemically pure uranyl acetate in water. The test solutions were made up in twice distilled water.

Uranium was determined in titanium-niobium and carbonate ores, and also in ores containing large amounts of phosphorus and iron.

Establishment of Optimum Conditions for Determining Uranium in Ores. The titanium-niobium ore dissolved readily in concentrated (anhydrous) phosphoric acid on heating. After dissolution of an aliquot, the solution acquired a green color which indicated that it contained mainly quadrivalent uranium. The light absorption maxima at 420, 480, 540, and 660 mμ are characterisitic of U^{IV} [21].

U^{IV} was oxidized to U^{VI} by addition of $K_2S_2O_8$ on heating. At the same time, during this stage, lead was precipitated from solution as $PbSO_4$ so that interference of large amounts of Pb^{2+} on the UO_2^{2+} peak was eliminated. Uranium was determined in this case in a supporting electrolyte of 1 M H_3PO_4 + 0.25 M K_2SO_4 [16]. In 1 M H_3PO_4 + 0.25 M K_2SO_4, UO_2^{2+} ions are reduced in one step [16]. Only one cathodic wave for uranium caused by reduction of U^{VI} to the quadrivalent state appeared on the current-voltage curve. Reduction is irreversible. In a phosphoric acid solution the current of the uranyl ions is directly proportional to their concentration. No anodic curve for uranium was detected in 1 M H_3PO_4 + 0.25 M K_2SO_4 [16].

It is clear from Table 1 that a number of accompanying elements do not interfere with uranium determination, since their peak potentials in phosphoric acid media are much more negative than E_p for UO_2^{2+}

TABLE 1. Effect of Accompanying Elements on I_p for UO_2^{2+} in 1 M H_3PO_4 + 0.25 M K_2SO_4

Accompanying elements, mg/ml		U taken, mg/ml	U found, mg/ml	Accompanying elements, mg/ml		U taken, mg/ml	U found, mg/ml
Fe^{3+}	0.24	0.12	0.12	Cu^{2+}	0.03	0.12	0.116
	0.60	0.12	0.12		0.06	0.12	0.088
	1.20	0.12	0.12	Pb^{2+}	0.12	0.12	0.12
Ti^{IV}	0.24	0.12	0.112	Nb^{V}, Ta, rare earths			
	0.60	0.12	0.117	1.20 each		0.12	0.12
	1.20	0.12	0.115				

The phosphoric acid concentration should not exceed 1 M. At higher phosphoric acid concentrations the titanium peak is shifted toward the positive side and almost fuses with the uranium wave. The sulfate ion concentration of the test solution should not exceed 0.25 M. At higher SO_4^{2-} concentrations the straight line relation between I_p and UO_2^{2+} concentration breaks down.

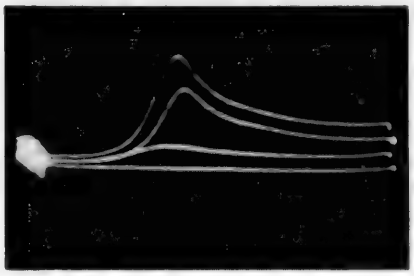

Fig. 1. Oscillogram of a phosphoric acid solution of a titanium-niobium-tantalum ore to which a standard solution of a UO_2^{2+} salt has been added. $U_{=}$ = +0.17 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec. Cathodic polarization.

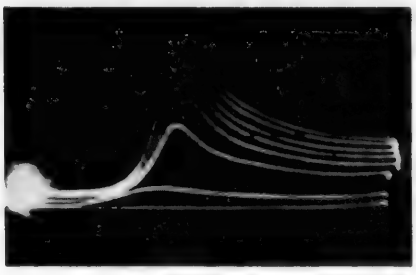

Fig. 2. Oscillograms of a phosphoric acid solution of a titanium-niobium-tantalum ore with five additions of a standard solution of a UO_2^{2+} salt. $U_{=}$ = +0.17 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec. Cathodic polarization.

An oscillogram of a phosphoric acid solution of a titanium-niobium-tantalum ore to which a standard solution of an uranyl salt has been added is shown in Fig. 1. A constant voltage $U_{=}$ = +0.17 v and a saw-toothed negative potential $U_{\sim}$ = 0.95 v were applied to the cell. The highest negative potential was -0.780 v. The rate of potential change was 1.3 v/sec, while a single sweep with a delay of 13 sec after the previous drop had broken off was used. The current of the supporting electrolyte—1 M H_3PO_4 + 0.25 M K_2SO_4—, the first curve from the bottom, is compared with the current of a solution containing test ore, the second from the bottom, in Fig. 1. The third curve is that of the UO_2^{2+} current after adding 0.235 mg of U to the test solution. The volume of the solution before addition of the standard solution was 3 ml. The bottom straight line is the zero line. The current for uranium is directly proportional to its concentration so that the the U content of the ore can be calculated by the method of additions (Fig.2). Fig. 2 was obtained under the same conditions as those used for Fig. 1. On this oscillogram the first curve from the bottom corresponds to the current for the supporting electrolyte 1 M H_3PO_4 + 0.25 M K_2SO_4. The second curve corresponds to the current of the solution containing the ore. The current-voltage curves 3, 4, 5, 6, and 7 were obtained after addition of successive portions of 0.1 ml of a standard uranyl salt solution to 3 ml of a phosphoric acid solution of the ore.

The straight line is the zero line (1 ml of standard solution contained 2.356 mg U).

Direct dissolution of ore in phosphoric acid followed by polarographic determination of uranium in this medium without preliminary chemical preparation appreciably speeds up determination. Nevertheless, because of the low solubility of the ore in concentrated H_3PO_4 (not more than 0.05 g in 1 ml) it was impossible, using the maximum sensitivity of the oscillographic polarograph, to determine less than 2% U in ores. The current of the supporting electrolyte, which fuses with the current of a solution containing very small amounts of uranium on the oscillogram, prevents one increasing the sensitivity.

In order to overcome this difficulty we increased the weight of aliquots of ore poor in uranium and decomposed them by fusion with $K_2S_2O_7$ [22]. The melt was dissolved in phosphoric acid and the uranium determined in a supporting electrolyte of 1 M H_3PO_4 + 0.25 M K_2SO_4. Ore poor in uranium was also decomposed by treating it with HF, removing F^- ions with nitric acid and determining the uranium in a supporting electrolyte of 1 N HNO_3.

Cathodic polarization of the electrode in a nitric acid solution of UO_2^{2+} gives only one cathodic wave on the current-voltage curve. Such a cathodic wave for UO_2^{2+} shown in Fig. 3 ($U_= = +0.08$ v; $U_\sim = 0.95$ v; V = 1.3 v/sec). A single sweep with a 13 sec delay after the previous drop had broken off was applied to the cell. The straight line is the zero line; the upper curve corresponds to the current for a solution containing 0.046 mg U/ml. The maximum current of UO_2^{2+} was measured from the supporting electrolyte curve to the maximum. For very low uranium contents in 1 N HNO_3 the current for the solution differs little from the current of the supporting electrolyte, so that the sensitivity with which uranium can be determined cannot be increased. Nevertheless, anodic polarization in the case of a nitric acid solution of an uranyl salt almost excludes the effect of the supporting electrolyte current on the peak of quinquevalent uranium (Fig. 4). The anodic curve of U in 1 N HNO_3 containing 4.6×10^{-2} mg U/ml is shown in the oscillogram in Fig. 4. Fig. 4 was obtained for $U_= = -0.5$ v; $U_\sim = 0.95$ v; V = 1.3 v/sec and for a single impulse with a delay of 13 sec after the previous drop had broken off. The sweep voltage was varied from -0.5 to +0.45 v. The middle curve – the current of the supporting electrolyte 1 N HNO_3 – intersects the zero line, and, at the more negative potentials, lies below the zero line. The upper uranium curve intersects the supporting electrolyte curve at $\varphi = -0.25$ v while that part of the curve which lies below the line of the supporting electrolyte is caused by reduction of UO_2^{2+} to UO_2^{+}. Since at the peak potential of the anodic wave ($\phi_p = -0.15$ v) the supporting electrolyte current coincides with the zero line, the anodic current was measured from the zero line to the maximum. The cathodic current was measured from the intersection point of the supporting electrolyte current with the zero line to the break in the wave located below the supporting electrolyte current. The current of the uranium anodic wave is equal to the sum of the cathodic and anodic currents measured in this way. The oscillogram in Fig. 4 znd Table 2 show that in the case of a nitric acid solution of a UO_2^{2+} salt, anodic polarization allows one to determine low concentrations of uranium in 1 N HNO_3 at the maximum sensitivity of the apparatus.

Fig. 3. Oscillogram for the cathodic wave of UO_2^{2+} in 1 N HNO_3. $U_= = +0.08$ v; $U_\sim = 0.95$ v; V = 1.3 v/sec.

Fig. 4. Anodic wave. U_V in 1 N HNO_3. $U_= = -0.5$ v; $U_\sim = 0.95$ v; V = 1.3 v/sec. U_{sweep} varied from -0.5 to +0.45 v.

The results given in Table 2 show that the value of the anodic peak of uranium is directly proportional to its concentration. The sensitivity of the method is 3×10^{-3} mg/ml.

The effect of accompanying elements on the value of the anodic peak of uranium was also studied in a nitric acid medium. It was established that most elements do not interfere with determination of uranium. The exception is trivalent iron which exhibits a strong influence on the maximum current of the anodic wave when its content in the solution is five times the uranium concentration.

TABLE 2. Relation between the Maximum Current of the Anodic Wave of Uranium and its Concentration in 1 N HNO_3. $U_= = -0.5$ v; $U_\sim = 0.95$ v; V = 1.3 v/sec. Single sweep. 13 sec delay after drop has broken off.

U, mg/ml	I_p, μa	U, mg/ml	I_p, μa
0,245	7,38	0,023	0,69
0,169	5,06	0,012	0,36
0,092	2,78	0,006	0,18
0,068	2,03	0,003	0,09
0,046	1,37		

The 1 N HNO_3 solution is suitable for determination of uranium in those ores which have been decomposed beforehand with a mixture of hydrofluoric and hydrochloric acids or with HF + HNO_3 (usually ores containing appreciable amounts of silica dissolve in a mixture of HF and HCl or HF and HNO_3). An ore containing a large amount of iron (about 70%) was decomposed with a mixture of HF and H_2SO_4; after removal of F^- and dissolving the residue in 0.1 N H_2SO_4, uranium was determined on the basis of the first cathodic wave [17]. Interference from Fe^{3+} was eliminated by addition of hydrazine sulfate. The oscillogram of

the ore containing appreciable amounts of iron, with two additions of standard solution of uranyl is shown in Fig. 5. The oscillogram was obtained during cathodic polarization using a single sweep and a 13 sec delay after the previous drop had broken off. $U_{=}$ = +0.02 v and $U_{\sim}$ = 0.95 v were applied to the cell; the rate of change in voltage was V = 1.3 v/sec. The sweep voltage was varied from +0.02 to -0.93 v. The first curve from the bottom corresponds to the current of the supporting electrolyte – 0.1 N H_2SO_4; the second, to the solution of the test ore; while the third and fourth waves correspond to a solution of the same ore with additions of standard uranium solution corresponding to 0.235 and 0.470 mg U/ml. The initial volume of the solution was 3 ml. It is clear from Fig. 5 that the maximum current of the uranyl ions in the 0.1 N H_2SO_4 containing the uranium from the ore is directly proportional to its concentration.

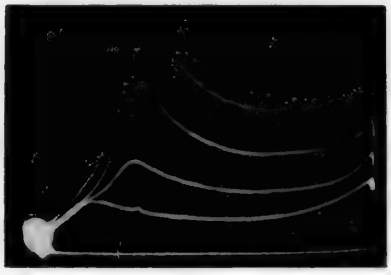

Fig. 5. Oscillogram of a sulfuric acid solution of an ore containing an appreciable iron content, to which two portions of a standard uranium solution have been added. The first cathodic wave of UO_2^{2+} ions was used. $U_{=}$=+0.02 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec.

Thus oscillographic polarography permits quantitative determination of uranium in some ores without preliminary separation of accompanying elements.

Experimental Procedure. Titanium-niobium-tantalum ores and also other ores soluble in concentrated phosphoric acid are analyzed as follows. 0.1-0.3 g of finely ground sample is dissolved on heating in 7 ml of H_3PO_4 (85%) contained in a 50-100 ml beaker. After dissolution is complete the solution has a green color; it is cooled and diluted 2-3 times with distilled water. After adding 3 g of $K_2S_2O_8$ the contents of the beaker are heated until the green color has disappeared and boiling is then continued for a further 3-5 min. After cooling, the solution is transferred to a 100 ml standard flask, diluted to the mark with water and carefully mixed. Three ml of this solution is transferred to the electrolyzer and an oscillogram taken at $U_{=}$ = +0.17 v and a negative saw-tooth voltage of -0.95 v. A single sweep with a 13 sec delay after the previous drop has broken off is applied to the cell. One determination takes less than one hour.

A titanium-niobium-tantalum ore containing less than 2% of uranium can be dissolved by fusing it with $K_2S_2O_7$. For this purpose a 1-2 g aliquot of ore is fused in a platinum or porcelain crucible with 6 g of $K_2S_2O_7$ for 30 min at 400-600°. The melt is leached with water on heating in a beaker, the solution is transferred to a 100 ml standard

TABLE 3. Determination of Uranium in Ores

Ore	Method used for decomposing the ore	Medium for uranium determination	Uranium found, %			
			by the method suggested*	chemically	radiometrically	x-ray spectrographically
Titanium-niobium-tantalum ore	Dissolved directly in H_3PO_4	1 M H_3PO_4 + 0.25 M K_2SO_4	11.40 11.40 11.40 11.28	10.50	11.36	11.50
Titanium-niobium-tantalum ore	Fusion with $K_2S_2O_7$	1 M H_3PO_4 + 0.25 M K_2SO_4	11.13 11.30 11.44 11.34	10.50	11.36	11.50
Titanium-niobium-tantalum ore	HF + HNO_3	1 N HNO_3	11.46	10.50	11.36	11.50
Carbonate ore	Fusion with $K_2S_2O_7$	1 M H_3PO_4 + 0.25 M K_2SO_4	0.073	0.070	–	–
Carbonate ore	HF + H_2SO_4	0.1 N H_2SO_4	0.069	0.070	–	–
Carbonate ore	HF + HNO_3	1 N HNO_3	0.072	0.070	–	–
Ore with high phosphorus content	Fusion with $K_2S_2O_7$	1 M H_3PO_4 + 0.25 M K_2SO_4	0.165	0.170	–	–
	HF + H_2SO_4	0.1 N H_2SO_4	0.174	0.170	–	–
Ore with high iron content	HF + H_2SO_4	0.1 N H_2SO_4	0.204 0.201 0.207	0.200	–	–

flask and 6-7 ml of 85% H_3PO_4 added; the volume is then made up to the mark with water. Three ml of this solution is transferred to the electrolyzer and an oscillogram is taken under the same conditions as those used when the ore is dissolved directly in concentrated H_2PO_4. One determination takes about two hours. When ores are decomposed with a mixture of HF and HCl or with HF + HNO_3 the residue is dissolved in 1 N HNO_3. Three ml of the solution obtained is introduced into the electrolyzer and anodic polarization carried out. $U_{=}$ = [illegible].5 v and a positive saw tooth voltage $U_{\sim}$ = 0.95 v are applied to the cell. An oscillogram of the anodic wave of uranium is obtained on the screen of the oscillographic polarograph using a single sweep and a delay of 10-13 sec after the previous drop has broken off.

Carbonate and phosphate ores low in uranium, and ores containing large amounts of iron can be analyzed as follows.

A 1-2 g aliquot of ore is placed in a platinum basin, and 10 ml of 40% HF and 6 ml of H_2SO_4 (sp.gr. 1.84) added. The contents are heated and then evaporated to dryness. Decomposition of the ore with the HF and H_2SO_4 mixture is repeated three times. The residue is cooled and then dissolved in 20-30 ml of 0.1 N H_2SO_4. Three g of hydrazine sulfate is added and the solution boiled for several minutes. The solution is cooled and transferred to a 50 ml standard flask. The volume of the solution is made up to the mark with 0.1 N H_2SO_4. Three ml of the solution obtained is introduced into an electrolyzer and oscillograms taken at $U_{=}$ = +0.02 v and $U_{\sim}$ = 0.95 v, using a single sweep with a delay time of 10-13 sec after the previous drop has broken off.

Whatever ore is analyzed the oscillograms of the supporting electrolyte, test solution, and solution to which a standard solution of uranium has been added are recopied on tracing paper, after which, using the usual method [19] the points are measured and the uranium content calculated by the method of additions. Results of determinations carried out by four methods are compared in Table 3; the methods used included the suggested method, Volkov's titrimetric method [23], radiometric, and x-ray spectrographic method [24].

The results in Table 3 show that oscillographic polarography permits determination of uranium in certain ores without preliminary removal of accompanying elements.

SUMMARY

It has been shown that oscillographic polarography is suitable for the determination of uranium in certain ores without preliminary removal of accompanying elements.

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SUCCESSIVE EXTRACTION PHOTOMETRIC DETERMINATION OF TRACES OF COPPER, NICKEL, IRON, AND MANGANESE

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Iron, copper, nickel, and manganese are widely spread impurities which are introduced into finished products from raw materials and constructional materials. The necessity of determining the content of these elements is determined by the fact that in the presence of microgram amounts of them the useful properties of many materials, e.g., those used in the production of scintillators and luminophors [1], deteriorate appreciably.

In the method which we should like to propose, copper, nickel, divalent iron, and manganese are extracted in succession from an ammoniacal-citrate buffer solution with diethyldithiocarbamate, dimethylglyoxime, 1-nitrose-2-naphthol, and diethyldithiocarbamate respectively.

The sensitivity of the reactions used is characterized by the data given in Table 1; the value of $\bar{\varepsilon}$ changes slightly on switching from one apparatus to another.

TABLE 1. Photometric Characteristics of the Complexes Used for Determination of Copper, Nickel, Iron, and Manganese

Compound	Molar extinction coefficient			"Mean" molar extinction coefficient (for the FEK-M apparatus)	
	λ, mμ	$\varepsilon \times 10^{-3}$	cited reference	FEK-M filter	$\bar{\varepsilon} \times 10^{-3}$
Copper diethyldithiocarbamate	436	12.8	[2]	blue	6.9
Compound of nickel with dimethylglyoxime in the presence of oxidizing agent	442	11.6	[3]	blue	8.8
Ferrous nitrosonaphtholate	690	16.0	[4]	red	12.0
Manganese diethyldithiocarbamate	400	3.8	[5]	blue	3.4

Copper ions are extracted with a solution of lead diethyldithiocarbamate in chloroform [6,7]. Only Ag^+, Hg^{2+}, Bi^{3+}, and Tl^{3+} interfere (the limiting ratios for 1 μg copper and for a maximum error of 20% are 1:500; 1:500; 1:4; and 1:10 respectively).

Nickel is separated by extraction of its complex with dimethylglyoxime with chloroform, followed by its transference to the aqueous phase and determination with dimethylglyoxime in the presence of an oxidizing agent [8]. Since copper has been removed beforehand there is no need to destroy the complex of copper with dimethylglyoxime.

Iron is separated and determined by means of the extraction photometric reaction of Fe^{2+} with 1-nitroso-2-naphthol which we had studied earlier [4] and which has a fairly high sensitivity. Apart from copper and nickel, of the usual metal ions only Co^{2+} and Ag^+ interfere with determination of iron (the limiting ratios for 5 μg ions are 1:4 and 1:10 for cobalt and silver respectively).

After removal of copper, nickel, and iron, only Co^{2+} and MoO_4^{2-}, which also form colored complexes, interfere with the determination of manganese in the form of its compound with diethyldithiocarbamate [9].

The order of separation adopted permits iron and manganese to be determined in the presence of 20 times their amount of MoO_4^{2-} and 10 times their amount of Co^{2+}.

Reagents, Solutions, and Measurement Technique. Solution of Lead Diethyldithiocarbamate in Chloroform. An aqueous solution containing 0.20 g of sodium diethyldithiocarbamate, 0.20 g lead nitrate, and 1 g sodium potassium tartrate is neutralized with ammonia to the phenol red color and shaken with chloroform. After being washed twice with two portions of water the extract is filtered and then diluted with chloroform to one liter.

Sodium diethyldithiocarbamate is purified by precipitating it from a saturated ethanolic solution with excess diethyl ether, after which it is dried in air [10].

Bromine water is prepared from analytical grade bromine purified by distillation.

Dimethylglyoxime (analytical grade), trisodium citrate (analytical grade), hydrochloric and sulfuric acids (chemically pure grade), perchloric acid (specially pure grade) were used. The remaining reagents and solutions were the same as those described in [4].

Metal salts were recrystallized; their solutions were acidified with sulfuric acid. The concentrations of the stock solutions of copper, nickel, and ferric sulfates, and manganese chloride containing 1000 μg of the metal per ml, were checked by titrimetric methods [11-13].

The optical density was measured on a FEK-M photoelectric-colorimeter relative to the solutions obtained in the control tests; the final volume was 24 ml in each case, a cuvette with a path length of 5 cm was used. The experimental results were treated statistically [14] at a confidence level of 0.95.

Experimental Procedure. An aliquot of preparation or preliminarily processed material is dissolved in water, to which is added 5 ml of an ammoniacal-citrate buffer solution (4% solution of trisodium citrate containing 5 ml of 0.1% phenol red per liter and neutralized with ammonia to the end point of this indicator) and if necessary, additionally neutralized with ammonia*. The solution is transferred to a 250 ml separating funnel and diluted to approximately 50 ml with water.

Determination of Copper. Copper is extracted twice with the solution of lead diethyldithiocarbamate in chloroform (5 ml portions), after which the solution is washed with 5 ml of chloroform and the washings combined with the extract. After diution with chloroform in a standard flask, the solution is filtered into the cuvette and the optical density measured using a blue filter.

Determination of Nickel. To the solution remaining after removal of copper is added 1-2 drops of ammonia (1:20), if necessary, until the appearance of the violet color of the indicator (pH ≥ 8.0). This is followed by 1 ml of dimethylglyoxime solution (1% solution in distilled aqueous alcohol); after 15 min the complex of divalent nickel with dimethylglyoxime is extracted with three portions of 5 ml each of chloroform. The combined extracts are shaken with three lots of 5 ml each of hydrochloric acid (0.5 N). 0.2 ml of bromine water, 1 ml of ammonia sp.gr. 0.91, and 0.5 ml of dimethylglyoxime solution are added to the hydrochloric acid solution obtained which has been placed in a standard flask, the volume of the solution is made up to the mark with water and the optical density measured after 15 min using a blue filter.

Determination of Iron. Fifteen ml of ascorbic acid (10% aqueous solution) is added to the solution remaining after removal of nickel, the solution is carefully neutralized with ammonia using phenol red as indicator, 5 ml of 1-nitroso-2-naphthol solution (1 g/liter to which 120 ml of 0.1 N KOH has been added per liter) is added and the volume made up to about 150 ml with water. After 45 min the complex of iron with 1-nitroso-2-naphthol is extracted twice with isoamyl alcohol (15 and 10 ml). The combined extracts are diluted with isoamyl alcohol in a standard flask and the optical density measured using a red filter.

Determination of Manganese. After removal of iron the solution is extracted with 10 ml of chloroform in order to remove any residual isoamyl alcohol. The chloroform layer is discarded, 5 ml of sodium diethyldithiocarbamate (5% aqueous solution) is introduced into the separating funnel and the whole shaken with 5 ml of chloroform. This last operation is repeated once again after which the solution is washed with a further 5 ml of chloroform. After dilution with chloroform in a standard flask the combined extracts are filtered into the cuvette and the optical density measured 15 minutes after mixing, a blue filter being used.

Calibration Curve. Calibration curves for the determination of copper, iron, and manganese were constructed

* The color transition range for phenol red is 6.8-8.0 pH units [15]; in practice, on careful neutralization with dilute ammonia (1:20) a pH value of 7.5 ± 0.5 is obtained under the conditions adopted.

by carrying out extraction of each metal ion from an ammoniacal-citrate buffer solution, following the procedures outlined above. The calibration curve for nickel was constructed by adding known amounts of Ni^{2+} to 15 ml of 0.5 N hydrochloric acid with subsequent addition of bromine water, ammonia, and dimethylglyoxime.

All four elements were found to conform quite well to Beer's law over the concentration range studied (from 0 to 20 μg of metal in 25 ml solution). The parameters of the calibration lines calculated by the method of least squares [14, 16] are given in Table 2.

TABLE 2. Parameters of the Calibration Lines: $D = \alpha + \beta C$ (C in γ/μg)

Metal determined	No. of experiments	$\alpha \cdot 10^3$	$\beta \cdot 10^2$
Cu	38	3.3±0.6	2.177 ± 0.006
Ni	33	4.1±0.4	3.010 ± 0.004
Fe	29	–	4.292 ± 0.007
Mn	30	–	1.247 ± 0.005

TABLE 3. Determination of Cu, Ni, Fe, and Mn in the Presence of Co^{2+} (50 μg) and MoO_4^{2-} (100 μg) (5 μg each of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} added). Number of experiments n = 3.

Test element	μg found in the presence of	
	Co^{2+}	MoO_4^{2-}
Cu	5.04 ± 0.32	4.96 ± 0.54
Ni	4.90 ± 0.25	4.93 ± 0.14
Fe	5.10 ± 0.25	5.13 ± 0.38
Mn	5.35 ± 0.81	5.00 ± 0.55

Effect of Foreign Ions. The number of metal ions which interfere with the determination of copper, nickel, iron, and manganese is very small. We though it would be interesting to acquire some quantitative results on the effect of Co^{2+} and MoO_4^{2-} on the results of the determinations of iron and manganese by this method. As the results in Table 3 show, relatively large amounts of these ions do not interfere with determination of the four elements in one aliquot.

Determination of Cu, Ni, Fe, and Mn in Alkali Metal Halides. The suggested method has been tried out on solutions containing known amounts of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} (up to 20 μg of each metal) and ammoniacal citrate medium. The results obtained are given in Table 4.

Analysis of potassium chloride and bromide for impurities can be carried out directly on an aqueous solution of the preparation, while in the case of sodium iodide and ammonium fluoride these salts must be converted into sulfate or perchlorate.

An aliquot of test material is placed in a 50-70 ml crucible (5 g NaI in a quartz crucible, 3 g NH_4F in a platinum crucible with a lid), and 5 ml of sulfuric acid in the case of NaI and 10 ml of perchloric acid in the case of NH_4F added. The crucible is heated on an electric hotplate with a power of 800-1000 watts, the heating element of the hotplate being covered with a piece of asbestos paper*. The same amount of acid is added to another crucible to serve as a control. The contents of the crucible are periodically shaken, the crucible being held on its outside with crucible tongs**. After evaporation of the iodine during decomposition of NaI, the acid in the crucible is evaporated further for 10-15 min. During decomposition of NH_4F, heating is continued for 40-50 min after perchloric acid vapors have started to come off.

The contents of the cooled crucible are dissolved in water, a drop of phenol red solution is added, followed by 5 ml of ammoniacal-citrate buffer solution and the whole carefully neutralized with ammonia solution sp.gr. 0.91 until the indicator color changes from red to straw-yellow (pH approximately 2). Neutralization of the solution obtained after decomposition of ammonium fluoride is carried out in a quartz beaker. The cooled solution is transferred into a 250 ml separating funnel and diluted to approximately 50 ml with water.

During analysis of KCl and KBr, 5 g of the preparation is dissolved in water to which 5 ml of ammoniacal-citrate buffer solution has been added.

The determination is completed according to the procedure outlined above.

When it is necessary to apply a correction to the experimental results, the iron content of the ammonia is periodically determined; for this purpose 50 ml of the latter is evaporated to dryness in a quartz beaker and the residue dissolved in water containing ammoniacal-citrate buffer solution.

Results for the determination of four elements in alkali metal halides are given in Table 5. In experiments

* A standard ceramic with a packed nichrome spiral is fixed on a ceramic base, e.g., a thick walled faced brick. A tube fitted onto a large glass funnel is fitted over the hotplate as a safeguard against dust.

** The ends of the tongs are protected with pieces of rubber tubing.

TABLE 4. Successive Determination of Cu, Ni, Fe, and Mn on one Aliquot

Metal determined / No. expt.	Cu			Ni			Fe			Mn		
	added, a_i (μg)	found x_i (μg)	$z_i = \frac{x_i}{a_i}$	a_i	x_i	z_i	a_i	x_i	z_i	a_i	x_i	z_i
1	10,0	10,52	1,052	5,26	4,51	0,857	10,0	9,60	0,960	10,0	9,78	0,978
2	—	—	—	—	—	—	10,0	9,11	0,911	5,0	5,92	1,186
3	1,0	1,06	1,060	5,26	5,68	1,080	10,0	10,21	1,021	—	—	—
4	—	—	—	5,26	5,11	0,971	—	—	—	5,0	4,41	0,882
5	1,0	0,87	0,870	5,26	6,18	1,175	10,0	9,55	0,955	5,0	5,85	1,170
6	1,0	1,01	1,010	5,26	5,45	1,036	10,0	9,55	0,955	—	—	—
7	1,0	1,24	1,240	1,05	0,80	0,762	1,0	1,33	1,330	—	—	—
8	1,0	1,01	1,010	1,05	1,04	0,990	1,0	0,93	0,930	2,0	2,57	1,285
9	1,0	1,19	1,190	1,05	0,94	0,895	1,0	1,07	1,070	2,0	2,16	1,080
10	1,0	1,19	1,190	1,05	0,97	0,924	1,0	1,00	1,000	2,0	2,32	1,160
11	10,0	10,52	1,052	10,53	10,70	1,016	10,0	9,44	0,944	10,0	9,54	0,954
12	10,0	10,47	1,047	—	—	—	10,0	9,67	0,967	10,0	9,94	0,994
13	20,0	19,48	0,974	21,06	20,29	0,963	20,0	20,04	1,002	20,0	20,21	1,011
14	20,0	19,52	0,976	21,06	20,55	0,976	20,0	19,87	0,994	20,0	19,41	0,971
15	5,0	5,01	1,002	5,26	5,30	1,008	5,0	4,87	0,974	5,0	5,13	1,026
16	10,0	10,20	1,020	10,53	10,66	1,012	10,0	9,69	0,969	10,0	9,78	0,978
No. expts. in	14			14			15			13		
z	1,050			0,976			0,999			1,052		
Dispersion $S^2 \cdot 10^3$	9,7			9,8			9,9			13,4		
Accuracy $\pm \delta_{0,95}$	0,057			0,057			0,055			0,070		
Error (relative) %	5,7			5,7			5,5			7,0		

TABLE 5. Determination of Cu, Ni, Fe, and Mn in Alkali Metal Halides Using One Aliquot (5 g of salt and 5 μg each of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} were introduced into the test sample, while the control sample contained 5 g of salt)

Preparation	No. of expts. in	Element determined	Mean arithmetic value of the values obtained	Dispersion $S^2 \cdot 10^2$	Accuracy $\pm \delta_{0.95}$	Error (relative), %
NaI	6	Cu	4,93	2,27	0,16	3,2
		Ni	4,95	3,10	0,18	3,6
		Fe	4,86	3,10	0,18	3,6
		Mn	4,88	12,43	0,37	7,4
KBr	5	Cu	5,23	7,64	0,34	6,8
		Ni	5,02	1,65	0,16	3,2
		Fe	4,99	8,19	0,35	7,0
		Mn	5,15	14,75	0,48	9,6
KCl	5	Cu	5,13	5,83	0,30	6,0
		Ni	4,93	3,44	0,23	4,6
		Fe	4,99	3,15	0,22	4,4
		Mn	4,97	1,74	0,16	3,2
NH_4F	5	Cu	5,00	0,61	0,10	2,0
		Ni	5,00	7,50	0,34	6,8
		Fe	4,88	5,70	0,30	6,0
		Mn	5,00	4,84	0,27	5,4

with NaI and NH_4F, the solution containing 5 g of the salt and measured amounts of Cu^{2+}, Ni^{2+}, Fe^{3+} and Mn^{2+} was evaporated to a minimum volume in a crucible, after which the residue was treated with H_2SO_4 or $HClO_4$. In experiments with KCl and KBr, the solution containing 5 g of the salt and measured amounts of each of the metals was introduced directly into the separating funnel. In all cases the control differed from the actual test only in that the solutions of the copper, nickel, iron, and manganese salts were replaced by the same volume of water; the control test was acidified with sulfuric acid like the test solutions.

SUMMARY

A method has been developed for the successive extraction photometric determination of traces of copper, nickel, iron, and manganese on one aliquot of high purity alkali metal halides (NaI, KBr, KCl, NH_4F, which are used for the production of scintillation and optical monocrystals.

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CHEMICO-SPECTROGRAPHIC DETERMINATION OF MICRO-IMPURITIES IN SODIUM AND POTASSIUM CHLORIDES AND IN TARTARIC ACID

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Chemico-spectrographic methods* are often used for the determination of impurities in those cases where the direct spectrographic method is not sensitive enough. Various chemico-spectrographic techniques have been described [1, 2]. The method of Solodovnik et al. [3] has been used very successfully on high purity acids.

The present article is devoted to a method based on conversion of the elements to be determined into sparingly soluble compounds, followed by precipitation of the latter on a collector and filtration of the collector from the solution. The dried collector plus impurities is then analyzed spectrographically.

In this way we** have determined tin, lead, cadmium, and bismuth present as impurities (of the order of 1×10^{-5}% each) in sodium and potassium chlorides, and also copper, cobalt, tin, lead, and silver in tartaric acid. As a basis for the determination of impurities in potassium and sodium chlorides we adopted a technique which we had developed earlier for chromic oxide, in which bismuth, tin, lead, and cadmium are coprecipitated on cupric sulfide formed on passing hydrogen sulfide into the solution [4]. Complete isolation of all the elements indicated above on the cupric sulfide was achieved by adding sodium diethyldithiocarbamate to the solution; sodium diethyldithiocarbamate has been successfully used previously both for analytical purposes [5], and also for purifying various salts from heavy metal impurities [6].

The enrichment process was carried out by different variants. Hydrochloric acid was added to the solution of sodium (or potassium) chloride (10 g in 50 ml of distilled water) containing the elements indicated above as impurities in amounts of 1×10^{-5}% each (in terms of the salt), until the pH was 3; 2.5 mg of copper as its sulfate was then added. Hydrogen sulfide was passed through the solution and 0.5 ml of a 1% aqueous solution of sodium diethyldithiocarbamate added. After two hours the cupric sulfide was filtered off through an ashless filter paper (1.5 cm diameter) on a Buchner funnel and washed with 5 ml of hydrogen sulfide water. The dry precipitate plus filter paper were burnt in an activated arc (220 v, 7.5 amps) using carbon electrodes (diameter of the cylindrical channel 4.2 mm, depth 6 mm). The spectra were photographed on an ISP-28 spectrograph fitted with a three lens slit illuminating system and a stepwise attenuator; the spectra were recorded on spectrographic photographic plates type II with a sensitivity of 16 units, using an exposure time of 2 min and a slit width of 0.015 mm.

* The terminology relating to chemico-spectrographic analysis has not yet been finalized. In our opinion, chemico-spectrographic methods involving collectors are characterized by the following indices: 1) the theoretical enrichment coefficient, which, calculated in terms of the test element, is the ratio of the weighable amounts of test sample and collector; 2) completeness of coprecipitation of the test impurity sorbed by the collector (as a % of the total content of the impurity in the test sample); 3) the coefficient of the increase in sensitivity of the determination, which is the ratio of the sensitivity obtained during a direct spectrographic determination to that obtained during a chemico-spectrographic determination.

This last index will, of course, change according to which direct spectrographic method is taken for comparison.

** I. A. Sviridkova took an active part.

The spectra of a "blank", those of the test sample and of three standards prepared from spectrographically pure cupric sulfide were taken 2-3 times on one photographic plate.

The following lines were measured photometrically on the spectra obtained:

Bi 3067.7; Pb 2833.1;
Sn 2839.9; Cd 2288.0.

Calibration curves were constructed within the coordinates S¬log C.

TABLE 1.

Element	Content of the element in the salt, %	Amount of element found in the salt, % (mean value)	Concentration of the element in the collector, %	Experimental error (relative), %
Bismuth	$1 \cdot 10^{-5}$	$1.18 \cdot 10^{-5}$	$2.6 \cdot 10^{-2}$; $4.3 \cdot 10^{-2}$ $3.4 \cdot 10^{-2}$; $3.4 \cdot 10^{-2}$ $3.8 \cdot 10^{-2}$; $1.8 \cdot 10^{-2}$ Mean $3.2 \cdot 10^{-2}$	+18
Tin	$1 \cdot 10^{-5}$	$0.92 \cdot 10^{-5}$	$1.4 \cdot 10^{-2}$; $1.4 \cdot 10^{-2}$ $5 \cdot 10^{-2}$; $2.6 \cdot 10^{-2}$ $3.2 \cdot 10^{-2}$; $1.3 \cdot 10^{-2}$ Mean $2.5 \cdot 10^{-2}$	-8
Cadmium	$1 \cdot 10^{-5}$	$1.11 \cdot 10^{-5}$	$1.7 \cdot 10^{-2}$; $4.8 \cdot 10^{-2}$ $2.4 \cdot 10^{-2}$ Mean $3.0 \cdot 10^{-2}$	+11
Lead	$1 \cdot 10^{-5}$	$0.9 \cdot 10^{-5}$	$2.5 \cdot 10^{-2}$; $3.0 \cdot 10^{-2}$ $2.3 \cdot 10^{-2}$ Mean $2.6 \cdot 10^{-2}$	-4

Similar results were obtained when another method was used, in which the collector was spectrographically pure cupric sulfide introduced into the solution in the form of finely ground powder. In this case, after adding sodium diethyldithiocarbamate to the solution, the latter was shaken and hydrogen sulfide passed through it.

A "blank" showed the absence of the lines of test elements in the spectrum. The theoretical enrichment coefficient was 2.7×10^3 in these experiments. It follows from this that the amount of the impurities in the collector, assuming that precipitation was 100% complete, should be $1 \times 10^{-5} \cdot 2.7 \times 10^3 = 2.7 \times 10^{-2}$.

Results of determinations by this method are given in Table 1.

Calibration curves for standards prepared from CuS are shown in Fig. 1; it is clear from these that the relation between S and log C is linear.

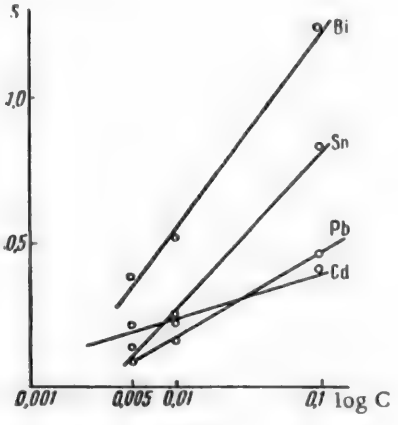

Fig. 1.

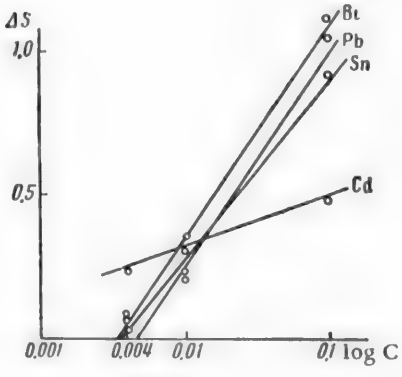

Fig. 2.

On using spectrographically pure carbon powder as collector and diethyldithiocarbamate as precipitant at pH 7.5, it was found possible to avoid the operation of passing hydrogen sulfide. On adding 0.025 g of carbon powder to a solution of NaCl or KCl under the conditions described above, such an analytical technique can only be used in those cases where the standards are prepared by enrichment from appropriate solutions of the salts with a known content of Bi, Sn, Cd, and Pb as impurities.

Under the conditions indicated above for carrying out spectrographic analysis a linear relation was obtained between $\Delta S = S_{impurity} - S_{background}$ and log C (Fig. 2) in this case. The cadmium line Cd 2265.0 was used instead of the line Cd 2288.0, since in the case of the latter the slope obtained for the curve was too small, probably, because of a self-rotation effect. This analytical variant enables one to use the "method of addition" successfully.

The sensitivity of this analytical technique is about 3.0×10^{-6}% for all the elements indicated above. At the same time, during direct determination, e.g., of Pb in sodium chloride, in an activated arc the sensitivity is 3×10^{-4}%. Thus the coefficient of the increase in the sensitivity of the determination is 1×10^{2}, while the theoretical enrichment coefficient is about 3×10^{3}.

Enrichment Process: the following solutions were prepared: a) 10 g of test tartaric acid was dissolved in 50 ml of distilled water; b) 10 g of the same material was dissolved in 41 ml of distilled water and the test elements added in amounts corresponding to the permissible norms for these elements as impurities, and the volume finally made up to 50 ml with distilled water.

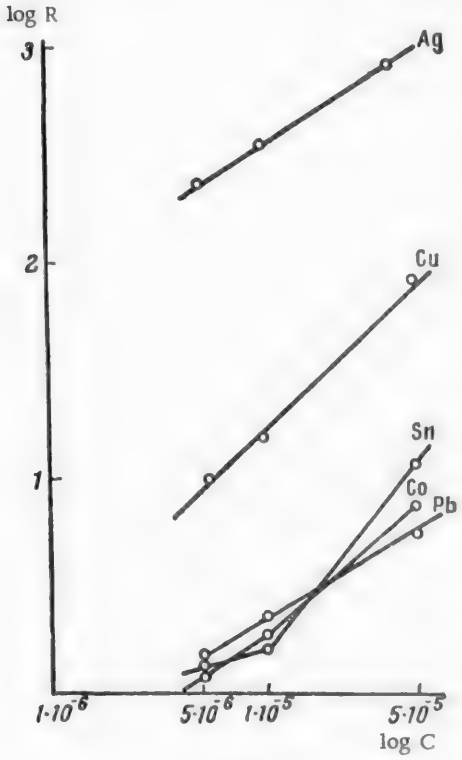

Fig. 3.

Chemically pure ammonia (25%) was then added to each solution until the pH was 5.5 (indicator paper).

Twenty mg of spectrographically pure carbon powder was added to each solution.

0.5 ml of 1% aqueous solution of sodium diethyldithiocarbamate is added at 30°* to each solution, the whole being carefully mixed by shaking, and then allowed to stand for 15 min. Hydrogen sulfide** is next passed through the solution for 5 min, and the precipitates filtered off through a 1.5 cm diameter ashless filter paper on a Buchner funnel; the precipitates are subsequently washed with an equal amount of water, and the pH adjusted to 5.5 with ammonia. The filter papers plus their precipitates are dried. The precipitates are then analyzed spectrographically. A "blank" is carried out (without tartaric acid) with the same amounts of reagents.

Determination is carried out on an ISP-28 spectrograph in a dc arc (220 v, 8 amps) with carbon electrodes. The lower electrode (anode) should have a cylindrical channel 4 mm deep and 4.2 mm in diameter. The upper electrode has a flat end face. A three-lens illumination system with a stepwise attenuator is used. All the precipitate (without the filter paper) is placed with 1 mg spectrographically pure NaCl [8] in the channel of the lower electrode. The spectra of the concentrates from solutions "a" and "b" and from the "blank" are photographed 2-3 times on one photographic plate. The exposure is 3 min at a slit width of 0.015 mm; photographic plates type 1.2 with a sensitivity of 8 GOST units are used.

The following lines are photometrically measured:

Co 3453.0; Ag 3280.7; Pb 2833.1
Cu 3247.0; Sn 2839.9.

* Ammonium bitartrate precipitate cannot be permitted.

** Hydrogen sulfide must be passed through the solutions to ensure complete precipitation of tin.

By measuring the blackening of these lines and the adjacent background the values of $\Delta S = S_{impurity} - S_{background}$ are found. The values of $\log \frac{I_{impurity}}{I_{background}}$ are then determined for all these spectra. After conversion to intensities the content of the impurities in the test sample is calculated by extrapolation using the "method of additions."

TABLE 2

Sample no.	Analytical method	Impurity content, %				
		cobalt	silver	copper	tin	lead
1	Chemico-spectrographic	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$2\cdot10^{-6}$	$7\cdot10^{-6}$	$4\cdot10^{-6}$
		$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$1{,}2\cdot10^{-6}$	$6{,}6\cdot10^{-6}$	$6\cdot10^{-6}$
	Chemical	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<3\cdot10^{-6}$	—	—
2	Chemico-spectrographic	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$4\cdot10^{-6}$	$1{,}0\cdot10^{-5}$	$1{,}2\cdot10^{-5}$
	Chemical	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<5\cdot10^{-6}$	—	—

The sensitivity of copper and silver determination is about 1.0×10^{-6}%, while that for the remaining elements is 3.0×10^{-6}%. Only about 0.003% of lead can be detected directly in tartaric acid using an activated arc.

Thus the coefficient of the increases in sensitivity of a determination in the case of lead is $1.0 \times 10^{+3}$, while the theoretical enrichment coefficient is 5×10^{2}.

The relation between log R (log of relative intensity) and log C is shown in Fig. 3; from this it is clear that over the concentration range 5×10^{-6} - 5×10^{-5}% it is only in the case of tin that an appreciable deviation from linearity is observed.

In order to establish the reproducibility of the method developed, parallel determinations were made of the relative intensity of the spectral lines of the test elements in one sample of tartaric acid. The following results were obtained.

	Cobalt	Silver	Copper	Tin	Lead
Maximum deviation of the intensity (%) from the mean value	±9	±21	0	±38	±6

Table 2 contains the results obtained by chemico-spectrographic and chemical methods for two samples of tartaric acid.

SUMMARY

A chemico-spectrographic method is suggested for the determination of 1×10^{-6} - 1×10^{-5}% of impurities in sodium and potassium chlorides (Sn, Pb, Cd, and Bi) and in tartaric acid (Co, Ag, Cu, Sn, and Pb).

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THE DETERMINATION OF WATER

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Among the numerous methods used for the determination of water content, methods based on the interaction of water with magnesium nitride and with calcium carbide and hydride have found wide application. The amount of water present is determined on the basis of the amount of ammonia, acetylene, and hydrogen respectively liberated. An essential feature in these cases is the relationship between the amounts of water present and the amounts of ammonia, acetylene, and hydrogen formed, the latter being dependent on the final reaction products. For example, during the reaction between water and magnesium nitride, $\frac{1}{3}$ or $\frac{2}{3}$ of a mole of ammonia will be liberated per mole of water, depending on whether the reaction follows equations (1) or (2).

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3, \quad (1)$$

$$Mg_3N_2+3H_2O=3MgO+2NH_3. \quad (2)$$

Similarly in the case of the reaction of water with calcium carbide and hydride, the relative amounts of water and acetylene or hydrogen will depend on the formation of calcium oxide or hydroxide as the result of the reaction:

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2, \quad (3)$$

$$CaC_2+H_2O=CaO+C_2H_2, \quad (4)$$

$$CaH_2+2H_2O=Ca(OH)_2+2H_2O, \quad (5)$$

$$CaH_2+H_2O=CaO+2H_2. \quad (6)$$

It is assumed in original papers and in textbooks [1-4] that the reactions between water and magnesium nitride, and calcium carbide and hydride are those given by equations (1), (3), and (5).

Bearing in mind the high reactivity of magnesium nitride, and calcium carbide and hydride, we assumed that these materials can react with the magnesium or calcium hydroxides formed according to equations (1), (3), and (5). Accordingly, interaction of water with Mg_3N_2, CaC_2, and CaH_2 with a quantitative yield of $Mg(OH)_2$ and $Ca(OH)_2$ according to equations (1), (3), and (5) in the presence of excess Mg_3N_2, CaC_2 and CaH_2 has a low probability.

We calculated the changes in the thermodynamic potentials for the reactions:

$$Mg_3N_2+3Mg(OH)_2=6MgO+2NH_3, \quad (7)$$

$$CaC_2+Ca(OH)_2=2CaO+C_2H_2; \quad (8)$$

$$CaH_2+Ca(OH)_2=2CaO+2H_2. \quad (9)$$

Table 1 contains the values of the thermodynamic potentials of all the compounds participating in reactions (7), (8), and (9).

We could not find any published values for the thermodynamic potential of magnesium nitride. We accordingly calculated this value from the known heat of formation of magnesium nitride (110.24 kcal [10]) and on the basis of the entropy of formations ΔS, calculated by Kireev's method [14] according to the formulas:

$$\Delta S_0=S-\Sigma n_{el}\,(S_{el})_i \quad (10)$$

$$\Delta S = \Delta S_0 - [\Sigma n_{el}\cdot S_{el} - \Sigma n_{el}\,(S_{el})_i]. \quad (11)$$

where: ΔS_0 is the entropy of formation of the compound from the elements found in the ideal state of a monoatomic gas; S is the entropy of the compound; n_{el} is the number of atoms of the given element in a molecule; S_{el} is the entropy of the element; and $(S_{el})_i$ is the entropy of the element in the state of an ideal monoatomic gas.

In order to calculate ΔS for magnesium nitride according to formula (11) we used the value of ΔS_0 for calcium nitride, a similar type of compound, calculated by means of formula (10).

TABLE 1. Thermodynamic Potential Values

Compound	ΔZ, 25°, kcal/mole	Literature cited	Compound	ΔZ, 25°, kcal/mole	Literature cited
CaC_2	— 16,2	[5]	CaO	—144,4	[6]
CaH_2	— 35,8	[6]	C_2H_2	+50,000	[8]
$Ca(OH)_2$	—214,33	[6]	NH_3	— 3,976	[9]
$Mg(OH)_2$	—199,27	[7]	Mg_3N_2	—95,5	—
MgO	—136,13	[7]			

The entropy values taken are given in Table 2.

$\Delta S_{0Ca_3N_2}$ = -159.21 electron units; $\Delta S_{Mg_3N_2}$ = -48,56 electron units, from which $\Delta Z_{Mg_3N_2}$ = -95.49 kcal/mole.

From the data given in Table 1 we find that

for reaction (7) ΔZ −131.42 kcal/mole; $K = 10^{96}$
for reaction (8) ΔZ −8.27 kcal/mole; $K = 1.1 \cdot 10^5$;
for reaction (9) ΔZ − 38.67 kcal/mole; $K = 2.5 \cdot 10^{27}$

It follows from this that reactions (7), (8), and (9) are almost irreversible. Possible inaccuracies in the determination of the value of $\Delta S_{Mg_3N_2}$ should not essentially effect the value of ΔZ for reaction (7) because of the large value of the latter.

Thus during determination of water by the nitride method for example, if the interaction of water with magnesium nitride goes to completion, calculation of the amount of water should be made in accordance with equation (2), not by equation (1) as is generally accepted at present. The possibility is not excluded of course that the reaction ceases with formation of magnesium hydroxide, as a result, for example of the slow rate of reaction (7).

TABLE 2. Entropy Values

Compound	S and S_{el} (25°)	$(S_{el})_i$ (25°)	Literature cited
Ca_3N_2	25	—	[11]
Ca	9,95	36,993	[6]
Mg	7,77	35,504	[12]
N_2	45,767	—	[13]
N	—	36,6147	[13]

The position is the same for determination of water by means of calcium carbide and hydride.

It is of interest to note that during water determination with calcium hydride, higher results are obtained for the water content in those cases where the samples interact with calcium hydride for a long time [15]. The author of [15] does not explain this fact but it is readily explained by the possibility that reaction (9) occurs. We have carried out some experimental checks using magnesium nitride as an example.

Experimental. We chose determination of water in dichlorodifluoromethane (Freon 12) as the subject of our study. According to GOST 8501-57 this determination is carried out as follows.

Magnesium nitride is placed in a U-tube and is purged with nitrogen dried over phosphorus pentoxide. After the U-tube with Mg_3N_2 has been purged it is connected to a cylinder of the test gas. Freon is then passed for one hour at the rate of 7-8 liter/hr over the magnesium nitride.

An absorption apparatus containing 3 ml of 0.01 N HCl is then connected between the tube and the gas counter. Three liters of Freon is then passed through at a rate of 7-8 liters/hr.

The NH_3 in the absorption solution is then determined photometrically with Nessler reagent. The water content of the Freon is then calculated by means of equation (1).

A check on this method showed that the experimental results of determinations carried out at different times are not reproducible. It was established that even samll variations in the temperature of the room in which the experiments were carried out appreciably affect the results.

A series of determinations according to GOST 8501-57 were carried out, but during this series the tube containing magnesium nitride was thermostatted. Results for two samples of Freon 12 over the temperature range 0-25° are given in Table 3.

In addition, sample No. 1 was also analyzed at 120° and 600°. The temperature of 120° was chosen in accordance with recommendations accepted in [1]. The water content was calculated according to equation (1). We chose 600° because at this temperature magnesium hydroxide is certain to decompose into MgO and H_2O.

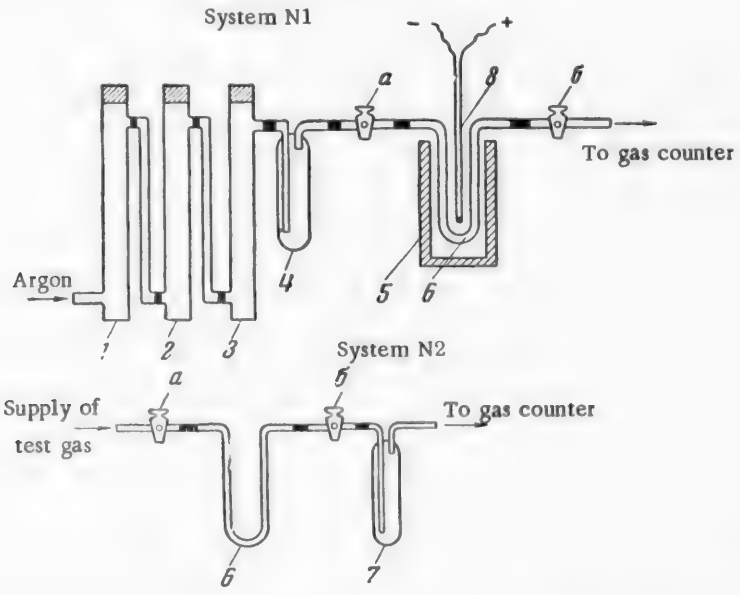
TABLE 3. Determination of Water in Freon at Different Temperatures

Temp, °C	H_2O found % wt.		Temp, °C	H_2O found % wt.	
	sample no.1	sample no. 2		sample no.1	sample no.2
0*	0,0019	—	20*	0,0034	0,0067
5*	—	0,0033	25*	0,0058	0,0089
10*	0,0038	0,0043	120*	0,0185	—
15*	—	0,0042	600**	0,0081	

* The amount of water was calculated by means of equation (1).

** The amount of water was calculated by means of equation (2).

The experiments at 120° and 600° were carried out as follows (see diagram).



Setup for the determination of water content at 600°. 1) Drying column of $CaCl_2$; 2 and 3) drying columns of P_2O_5; 4) trap; 5) oven; 6) quartz tune with Mg_3N_2; a,b three-way taps; 7) absorber containing 0.01 N H_2SO_4; 8) thermocouple.

The nitride containing tube was purged at the temperatures indicated at the rate of 7-8 liters/hr with argon carefully dried over P_2O_5. Purging at 120° was carried out until the ammonia content of the argon after passing through the nitride tube had dropped to 5 μg/liter, and had dropped to zero at 600°.

An absorption apparatus containing 3 ml of 0.01 N H_2SO_4 was then connected between the nitride tube and the gas counter, and 3-5 liters of the test Freon and two liters of dried argon passed in succession through the nitride tube.

Purging of the nitride tube with argon is essential for removal of Freon. Otherwise, as experiment showed, very high results are obtained as a result of the interaction of Freon with magnesium at the high temperatures used with liberation of ammonia. After removal of Freon the nitride tube was placed in an oven heated to 120 or 600° respectively and purged with 5 liters of dried argon.

The amount of ammonia in the absorption solution was determined with Nessler reagent on a FEK-M photocolorimeter.

From a comparison of the experimental results obtained at 120 and 600° it follows that magnesium nitride reacts quantitatively with water even at 120° according to equation (2) and not according to equation (1) as Isakov et al. considered [1].

TABLE 4. Results for the Determination of Water in Nitrogen

Mg_3N_2		P_2O_5	Mg_3N_2		P_2O_5
t=600°	t=22–23°	H_2O, % wt.	t=600°	t=22–23°	H_2O, % wt.
H_2O, % wt.	H_2O, % wt.		H_2O, % wt.	H_2O, % wt.	
0,026	0,014	0,024	0,031		
0,028	0,011	0,024	0,032		
0,027	0,0103	0,028	0,0325		
0,032	0,011		0,0326		
0,0268	0,012				

It is also clear from Table 3 that determination of the water content by GOST 8501-57 is not feasible, since the results are sharply dependent on the temperature of the magnesium nitride.

It should also be noted that calculation of the water content according to equation (1) should give high results. Meanwhile it is clear from Table 3 that the results obtained are low. This can be explained by adsorption of ammonia by magnesium nitride.

In order to confirm the correctness of the suggested method for determining the water content of the gas, a series of determinations of water contents was carried out by two methods; 1) by means of Mg_3N_2 at 600°; 2) with phosphorus pentoxide.

In the second method the water content was determined from the increase in weight of an absorption tube containing phosphorus pentoxide after a known amount of the test gas had been passed through the pentoxide.

Results of these determinations are given in Table 4. Results obtained on using GOST 8501-57 at 22-23° are also included in the table for comparison.

The results given in Table 4 confirm that the GOST 8501-57 method gives incorrect results, and demonstrate the satisfactory reproducibility of determinations carried out with magnesium nitride at 600° and the agreement of these results with those obtained on using phosphorus pentoxide.

SUMMARY

It has been shown that the methods commonly used for the determination of water on the basis of the amounts of ammonia, acetylene, and hydrogen liberated during the interaction of water with Mg_3N_2, CaC_2, and CaH_2 respectively, and which are based on the assumption that the interaction proceeds according to the equations:

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3,$$
$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2,$$
$$CaH_2+2H_2O=Ca(OH)_2+2H_2,$$

are erroneous. The interaction of e.g. Mg_3N_2 with the same amount of water can give rise to different amounts of ammonia depending on the temperature. In particular the method of determining water in Freon 12 by means of GOST 8501-57 is incorrect.

A method of determining water with Mg_3N_2 is suggested which is based on carrying out the reaction at 600°; this ensures that ammonia is formed stoichiometrically according to the equation $Mg_3N_2 + 3H_2O = MgO + 2NH_3$.

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BRIEF COMMUNICATIONS

DETERMINATION OF SEXIVALENT CHROMIUM IN CATALYSTS FOR OLEFIN POLYMERIZATION

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A chromium catalyst prepared by impregnating alumino-silicate with chromium trioxide is used for the polymerization of olefins [1-3]. During its heat treatment, with the aim of dehydrating the alumino-silicate, the chromium trioxide undergoes a stepwise loss of oxygen with formation, apparently, of chromium and aluminum chromates [4,5].

The generally known iodometric method of determining sexivalent chromium only permits determination of water soluble chromium ions in the chromium catalyst, and not chromium in the form of chromium chromate and aluminum chromate because of the insolubility of these chromates in water.

During a study of the effect of chemical composition on the activity of a chromium catalyst the problem arose of developing a method which would permit determination of sexivalent chromium in water-insoluble chromates. The method which we would like to suggest for determination of sexivalent chromium is based on the capacity of CrO_3 (independent of what form it is in) to liberate oxygen on heating ($2CrO_3 \rightarrow Cr_2O_3 + 3O$) and on its subsequent entertainment. There are published references to the determination of oxygen in inorganic compounds, e.g., in zinc oxide [6] by its reduction with carbon:

$$ZnO + C = Zn + Co.$$

The carbon monoxide liberated is determined by different methods. Korshun [7] adopted the principle of this method for direct determination of oxygen in organic compounds. The method is based on decomposition of the organic compound and trapping the oxygen in the form of CO_2 which is obtained by oxidizing CO with iodine pentoxide. It was suggested subsequently that cupric oxide be used for oxidizing CO to CO_2 [8].

Essentially, as applied to chromium catalysts, the method consists in heating the products of thermal decomposition (at 900° for 3 hr) of chromium trioxide with platinum black in an inert gas current. The oxygen, formed as the result of the thermal decomposition of the catalyst, is quantitatively converted into CO. The latter is passed through cupric oxide at 380°, the monoxide is thereupon oxidized to CO_2; the CO_2 is determined from the increase in weight of askarite. The amount of CO_2 formed should not exceed 4-5 mg; accordingly the weight of catalyst taken (weighed on a microbalance) should be 20-30 mg. The apparatus used for determination of oxygen in the catalyst is shown in Fig. 1 in M. O. Korshun and N. E. Gel'man's book [9]. The nitrogen in which the determination is carried out must be purified very carefully.

The content of sexivalent chromium is calculated from the amount of oxygen formed and the carbon dioxide obtained on heating the catalyst.

The alumino-silicate used as carrier still contains 1.5-2% of water (as determined from the loss in weight of the alumino-silicate on calcining to 1200°) even after thermal treatment at 500°. This water decomposes during the determination with liberation of oxygen, which, at 1000° in the presence of platinum black, forms CO and then CO_2. Accordingly, the oxygen content of the alumino-silicate carrier must be determined.

The amount of sexivalent chromium is calculated by means of the formula

$$\%Cr^{VI} = \left(\frac{B' - x}{a'}\right) - \left(\frac{B - x}{a}\right) \cdot 36{,}36 \cdot 2{,}1666 = \left[\frac{(B' - x)}{a'} - \frac{(B - x)}{a}\right] \cdot 78{,}78,$$

where B' is the increase in weight of the askarite, mg (corresponding to the amount of CO_2 formed on heating the

chromium catalyst); B is the increase in weight of the askarite, mg (the amount of CO_2 formed on heating the alumino-silicate); a' and a are respectively the weight (g) of the catalyst and alumino-silicate; 0.3636 is the conversion factor O/CO_2; 2.1666 is the conversion factor $2Cr/O_3$; and x is the increase in weight of the askarite in the blank.

TABLE 1. Determination of Cr^{VI} in Chromium Oxides by the Thermal Decomposition Method

Oxide*	Amount, %				Cr^{VI} found iodometrically, %
	active oxygen		Cr^{VI}		
	theoretical value	determined experimentally	theoretical value	determined experimentally	
CrO_3	24	24.2	52.00	52.43	52.2
$Cr_2(Cr_2O_7)_3$ dichromate	18.80	18.60	40.73	40.29	30.0
$Cr_2(CrO_4)_3$ monochromate	15.92	15.98	34.49	34.62	0
Chromium oxide Cr_2O_3	absent				

Note. Chromium oxides, and dichromate and monochromate, and chromium oxide were prepared from $Cr(OH)_3$. Their composition was checked by a differential thermal method, thermogravimetrically, and by x-ray analysis*.

TABLE 2. Determination of Cr^{VI} in a Chromium Catalyst (Heated beforehand at 500°)

Chromium content, %	Cr^{VI} found in the catalyst, %		By the method developed
	iodometrically	notes	
3-4	1.70	1.68	Mean values of two determinations.
5-6	3.55	2.77	
6-8	5.00	4.00	

The method of determining sexivalent chromium on the basis of the oxygen content was checked on a series of chromium oxides (Table 1).

The mean results of two determinations are given in the table.

As Table 1 shows, the iodometric method of determining Cr^{VI} gives low results for water-insoluble oxides.

The results in Table 2 show that the results obtained by the two methods of determining Cr^{VI} agree with each other, as long as the catalyst does not contain more than 4% of chromium.

The method developed makes it possible to follow those changes which the catalyst may be subjected to during reaction, by determining both the water soluble and water insoluble sexivalent chromium in it.

SUMMARY

A method has been developed for the determination of chromium (VI) in a chromium catalyst used for olefin polymerization; it is based on the capacity of CrO_3 to liberate oxygen on heating. The amount of Cr (VI) in the catalyst is calculated from the amount of oxygen evolved and the equivalent amount of carbon dioxide formed from it.

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A NEW PHOTOMETRIC METHOD FOR DETERMINATION OF VANADATES

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We have developed qualitative and quantitative methods for determination of vanadates which are based on the interaction of vanadates with α-naphthylamine in the presence of oxalate ions in a weakly acid medium, with subsequent extraction of the blue reaction product with n-butanol. Fe^{3+}, Ti^{4+}, Mo^{VI}, W^{VI} and other ions do not interfere. Popov [1] was the first to use α-naphthylamine in the presence of nitric acid (1:3) for detecting vanadates. This reaction has not been used for quantitative determination.

Vanadates are detected as follows: one drop of test solution and 4-5 drops of n-butanol are added to a mixture consisting of one drop of 0.1-0.5 N ammonium oxalate solution, one drop of 0.5-2 N sulfuric acid, and one drop of an acetic solution of α-naphthylamine (2 g/liter). A blue color which rapidly changes to violet in the n-butanol layer indicates the presence of vanadates in the test solution. The limit of identification is 4 μg of vanadate ion; the limiting dilution is 1:40,000.

The optical density of the extracts obtained is measured for quantitative determination. A standard series is prepared as follows in order to construct a calibration curve. Vanadate solution is measured out of a microburet into a measuring cylinder, the amount taken being such that the vanadate ion content is not less than 0.1 mg. One ml of α-naphthylamine solution (2 g/liter), five drops of 2 N sulfuric acid, and five drops of 0.5 N ammonium oxalate solution are then added. The solution obtained is diluted to 5 ml with water. After 5 min the colored compound is extracted four times with n-butanol. The extracts are transferred to a measuring cylinder which can be drained from the bottom, the water is allowed to drain off and the volume of the butanol layer made up to 10 ml.

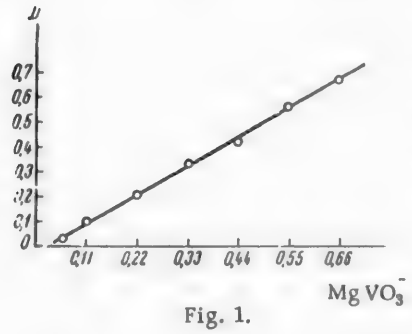

Fig. 1.

The optical density is measured 40-60 minutes after extraction, a FEK-M photocolorimeter fitted with a green filter being used. The extracts confirm to Beer's law (Fig. 1).

TABLE 1. Determination of Vanadium in Synthetic Mixtures

Mixture No.	Content of other ions, mg	VO_3^- taken, mg/10 ml	VO_3^- found, mg/10 ml	Error (relative), %	Mixture No.	Content of other ions, mg	VO_3^- taken, mg/10 ml	VO_3^- found, mg/10 ml	Error (relative), %
I	Fe^{3+} – 100	0.110	0.113	+2.73	III	MoO_4^{2-} – 50	0.110	0.112	+1.8
		0.330	0.328	-0.61			0.330	0.330	0.00
		0.550	0.554	+0.73			0.550	0.547	-0.55
II	WO_4^{2-} – 50	0.110	0.108	-1.8	IV	Ti^{4+} – 50	0.110	0.115	+4.5
		0.330	0.326	-1.21			0.330	.0325	-1.5
		0.550	0.547	-0.55			0.550	0.555	+0.91

Vanadate ions were determined by this method in synthetic mixtures in the presence of Fe^{3+}, WO_4^{2-}, Ti^{4+} (Table 1), and also in various marks of steel (Table 2). An aliquot of test material was dissolved by the usual method [2]. $KMnO_4$ was used for oxidizing quadrivalent vanadium, excess $KMnO_4$ being removed with sodium nitrite. Excess

nitrite was removed with urea. The solution obtained was quantitatively transferred to a standard flask.

TABLE 2. Determination of Vanadium in Steels

Mixture No.	V content, %	V content, %	Error (relative), %	Mixture No.	V content, %	V content, %	Error (relative), %
1	0.240	0.242	+0.83	2	0.30	0.295	-1.66
	0.240	0.239	-0.42		0.30	0.310	+0.34
	0,240	0.237	-1.22	3	1.39*	1.32	-5.02
2	0.30	0.300	±0.00		1.39*	1.38	-0.72
					1.39*	1.41	+1.44

* The steel contains 17.68% W.

SUMMARY

A phtocolorimetric method has been developed for the determination of vanadates; it is based on the interaction of vanadate with β-naphthylamine in the presence of oxalate ions in a weakly acid medium.

Iron (III), titanium, molybdenum (VI), and tungsten (VI) ions do not interfere with vanadium determination.

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COMPLEX FORMING REACTIONS BETWEEN FERRIC IRON AND MANNITOL

A. V. Pavlinova and N. M. Cherkasova

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 733-735, November-December, 1961
Original article submitted August 24, 1960

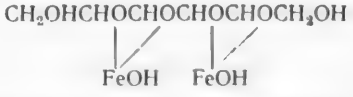
It is suggested in Nikitina's textbook [1] that iron can be complexed with mannitol during the titrimetric determination of aluminum with tartrates. No information is given on the composition and properties of the complex formed with mannitol. Consequently we decided it would be interesting to study this complex formation reaction.

The fact that complex formation does not occur is indicated by the intense yellow color of an iron salt solution after addition of mannitol, and by the fact that ferric hydroxide is not precipitated on adding alkali until the pH is 9. During this reaction it is essential to take a large excess of mannitol: for a 0.1 N solution of an iron salt a six-fold excess is taken, while for a 0.015 N solution a sixteen-fold excess is necessary. A considerable amount of alkali is used up in neutralizing the solution of mannitol and iron salt. In order to determine this amount and in order to choose an indicator for titration, three solutions were prepared, each containing 0.000473 g·mole of $FeCl_3$, and 0.00149, 0.00528, and 0.01056 g·mole of mannitol respectively. Titration curves were constructed for each solution (Fig. 1). 0.4736 N alkali was used as titrant. pH was measured on a LP-5 potentiometer using calomel and glass electrodes.

Fig. 1 shows that solutions containing ferric iron and mannitol titrate like strong acids. Excess mannitol does not affect either the nature of the curve or the amount of alkali used. During this titration three equivalents of acid correspond to 1 gram atom of iron (3 ml of 0.4736 N alkali was used up on 0.000473 g·atom of iron, i.e., 0.00142 g·eq).

A precipitate separates out in all cases at pH of about 5, but it dissolves on further addition of alkali until the pH is about 9. In appearance the precipitate is reminiscent of basic iron salts; it contains iron and carbon (CO_2 is liberated on calcining with cupric oxide). The compound of iron with mannitol separates out in the form of a yellowish-brown precipitate which is very fine and is difficult to filter. On drying in air the volume of the precipitate decreases considerably and it darkens; it is sparingly soluble in water but dissolves readily in alkali.

A precipitate which was separated in a large volume of alcohol was washed with 50% ethanol to remove excess mannitol was dried at 105° and then calcined in a muffle furnace. The residue left after calcination was dissolved in hydrochloric acid, and the iron determined gravimetrically. Carbon was determined on a separate aliquot by calcining with cupric oxide and absorbing the CO_2 with alkali. 22.11% Fe and 15.75% C were found; these values correspond to a ratio of Fe: mannitol of 2:6, i.e., one molecule of mannitol corresponds to 2 atoms of iron. This suggests that the following compound is formed:



The precipitate does not loose all the water at 105°; an appreciable fraction of it is liberated at higher temperatures. The following results were obtained after introducing a correction water:

Found: 32.95% Fe; 23.36% C; 45.90% loss on calcining
Calculated: 34.57% Fe; 22.22% C; 50.61% loss on calcining

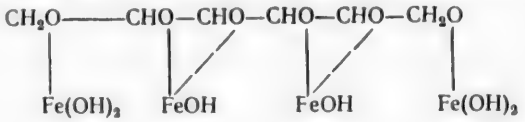
In order to determine the composition of the compound formed on increasing the pH, and to dissolve the precipitate, the latter was precipitated from an alkaline solution (pH about 9) by addition a three-fold amount of ethanol (96%). In order to check on the purity of the precipitated compound, it was reprecipitated with ethanol. The analytical results obtained before and after reprecipitation are given below:

Found before reprecipitation 43.16% Fe; 14.74% C; 41.36% loss on calcining

Found after reprecipitation 43.31% Fe; 14.66% C; 43.04% loss on calcining
Calculated 44.62% Fe; 14.34% C; 42.22% loss on calcining

It is clear that the composition of the compound does not change on reprecipitation; this indicated that the compound has an individual character.

From the results obtained we find: Fe:C = 4:6.3, or 4:6. The compound has the formula:



Ferric hydroxide is not precipitated in a weakly acid medium (pH > 3) in the presence of mannitol; this indicates that complex formation starts even in an acid medium. In order to determine the composition of the compound formed under these conditions, mixtures of solutions of an iron salt and mannitol prepared by the isomolar series method were examined potentiometrically. The total concentration was the same for one series of experiments and equal to 0.0985 M. while it was 0.2735 M in another. The curves obtained are shown in Fig. 2. The composition of the mixture is plotted along the abscissa while the voltage in millivolts is plotted along the ordinate. A break corresponding to a ratio of Fe: mannitol = 2:3 is observed on both curves.

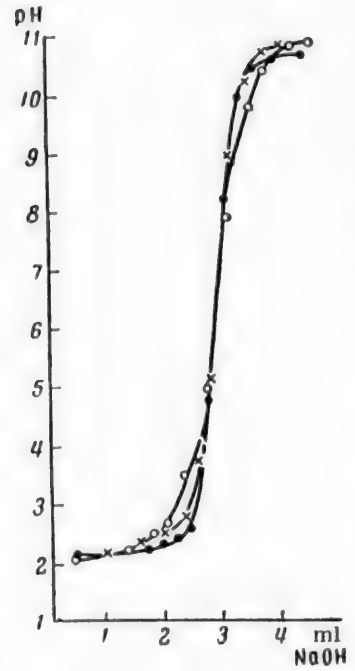


Fig. 1.

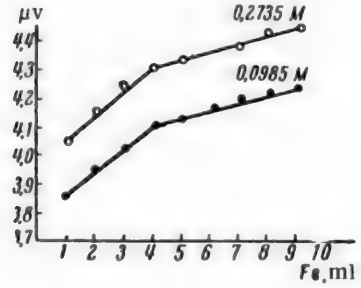


Fig. 2.

It has been established therefore that three complexes are formed between mannitol and iron: Fe_2Man_3 (where Man is mannitol) in an acid medium; $Fe_2(OH)_2Man$ in weakly acid and neutral media; and $Fe_4(OH)_6Man$ in alkali media. Complex formation proceeds stepwise, while the amount of hydroxyl groups whose hydrogen is substituted by iron increases with increasing pH.

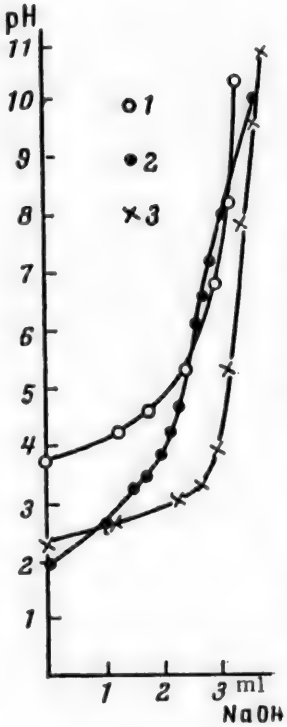


Fig. 3.

In order to examine the interaction of the mannitol complex of iron with potassium tartrate we constructed titration curves of the tartrate complex of iron with alkali in the presence of and in the absence of mannitol. In one case 10 ml of potassium sodium tartrate 0.367 M was added to 10 ml of 0.2735 M $FeCl_3$ solution, while in the second case 10 ml of mannitol 0.565 M was added, and in the third 5 ml of potassium tartrate and 5 ml of mannitol were added.

The titration curves are shown in Fig. 3.

It is clear from Fig. 3 that the tartrate complex of iron (curve 1) titrates as a weaker acid than the complex with mannitol (curve 3). After addition of equal volumes of potassium sodium tartrate and mannitol, curve 2 is obtained, which lies between curves 1 and 3 and is more similar in character to the curve for the tartrate complex of iron. It can be deduced from this that some of the iron atoms change over from mannitol to tartrate.

The results obtained helps one to explain the processes which occur during titration of aluminum by E. I. Nikitina's method.

According to this method aluminum is determined from the difference between the two volumes of alkali used in titrating a solution containing mannitol and potassium sodium tartrate, and the same volume of solution containing mannitol and sodium oxalate. In the first instance, the free acid, acid liberated during the interaction of iron with

mannitol, and acid liberated during the interaction of aluminum with potassium sodium tartrate are titrated. In the second case the free acid and the acid from the reaction of iron with mannitol are titrated, since oxalate complexes aluminum as a neutral complex. E. I. Nikitina is of the opinion that in the second titration only the free acid is titrated. In fact, as our experiments have shown, iron liberates an acid with mannitol which is also titrated. But, since equal volume of solutions are taken for both titrations, while mannitol is added to each, this does not reflect on the difference in the volumes. Accordingly, mannitol does not affect determination of aluminum. In a solution containing potassium sodium tartrate, the mannitol complex partially breaks down and changes into a tartrate complex. But this does not affect the amount of acid liberated, since three equilvalents of acid are also liberated during formation of the tartrate complex [2].

SUMMARY

It has been established that iron forms three complexes with mannitol: Fe_2Man_3 in an acid medium, $Fe_2(OH)_2Man$ in weakly acid and neutral media, and $Fe_4(OH)_6Man$ in an alkaline medium (where Man equals mannitol).

It has been shown that iron can be titrated with alkali in the presence of excess mannitol using phenolphthalein as indicator, the solution being clear at the titration end point. The color of the indicator is readily observable; three equivalents of acid are titrated per iron atom.

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2. A. V. Pavlinova, Zh. analit. khimii 3, 7 (1948).

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DETERMINATION OF RHENIUM IN COAL

V. V. Kuznetsova

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Original article submitted February 1, 1961

Goldsmith and Peters [1], Ratynskii [2], Headlee and Hunter [3], Fuchs [4] and others have shown that coal ash, particularly brown coal ash, often contains appreciable amounts of vanadium, molybdenum, uranium, germanium, and nickel. During endogenic processes rhenium, a scattered element with a Clark number 1×10^{-7}%, always accompanies molybdenum. Normal methods cannot be directly used for determination of rhenium in coal containing appreciable amounts of molybdenum. The basic difficulties involved in this case are connected with the very high volatility of rhenium oxides (Re_2O_7 volatilizes at 157°) [5], which leads to loss of rhenium. Experiment has shown that on ashing coal, up to 50% of rhenium is lost (Table 1). Aliquots of coal contained in porcelain crucibles were placed in a cold muffle furnace and the temperature taken up to 500-800°. Rhenium was determined in the ash by the thiocyanate photometric method [6].

On the basis that the stability of perrhenates is considerably higher than the stability of rhenium sulfides and oxides [5], we tried to combine ashing with sintering during the usual method of determining rhenium in sulfides and rocks [6].

To aliquots of coal (10 g) free from rhenium was added 20 g of CaO and 50, 20, 20, and 5 μg of rhenium. After sintering 600°, 48, 22, 18.5 and 5 μg of rhenium were found.

It is clear that in the presence of calcium oxide the decomposition temperature can be raised to 600-650° without any danger of loosing rhenium. At this temperature, and on adding potassium permanganate as oxidizing agent, the organic matter in the coal is oxidized while the rhenium and molybdenum form stable calcium perrhenate and molybdate. In order to ensure oxidation of organic residue, bromine water was added during the leaching process. Rhenium was determined photometrically in the form of its thiocyanate complex after removal of molybdenum with potassium butylxanthogenate in chloroform. At this stage, however, we came up against a new difficulty. Frequently, during analysis of natural coal, instead of the characteristic yellow colors of the thiocyanate complex of rhenium, we obtained yellow-green colors which could not be compared with the color of standard solutions. Such colors may be the results of high concentrations of vanadium, tungsten, niobium, chromium, and nickel [7-9]. Addition of citric or tartaric acid which complex tungsten into a colorless tartrate or citrate did not destroy the interfering color.

TABLE. 1. Loss of Rhenium during Ashing of Coal (Rhenium was added together with MoS_2)

Aliquot of coal free from rhenium, g	Re added, μg	Re found in the ash, μg	Loss of Re, %	Ashing temperature
5.1	10	6.4	36	500
5.4	10	5.6	44	800
10.0	50	28.3	43.4	500
10.2	50	24.5	51	800

Spectrographic analysis indicated that in addition to tungsten, the test coal samples contained appreciable amounts of vanadium (up to 0.11%), while the content of the remaining elements listed above did not exceed a few thousandths of a percent. The problem therefore reduced to making the green color of the vanadium thiocyanate compound. It is known [7] that vanadium, together with titanium, chromium, etc. forms a colorless complex with fluoride ions. Accordingly, in order to remove the green color caused by the vanadium, sodium fluoride solution was added (Table 2).

Analytical Procedure. An aliquot of about 20 g of coal is carefully mixed in a porcelain basin with 40 g calcium oxide and 1 g of potassium permanganate. A further 5 g of calcium oxide is strewn over the mixture. The crucible and its contents are placed in a cold muffle furnace, preferably with an air draught, and the temperature

gradually taken up to 600°. The sample is sintered at this temperature for 6-8 hr. The sinter is leached by heating for about 2 hr on a water bath with water to which a few ml of bromine water has been added. The solution is filtered through a porous filter and the precipitate on the filter washed several times with hot water. The filtrate is evaporated into a 100 ml separating funnel. The volume of filtrate plus wash liquor should be about 30 ml.

TABLE 2. Effect of Sodium Fluoride on the Results of Determining Rhenium in the Presence of Vanadium

Introduced		5% NaF solution added, ml	Re found, μg	Note
V	Re, μg			
100 μg		5		Weak yellow-green color disappears after addition of NaF
1000 μg	50	10	51	
1000 μg	50	10	48	
10 mg	–	10 μg	–	Yellow-green color disappears 10-15 min after addition of NaF
10 mg	50	10	51.5	
30 mg	50	10	49	
30 mg	50	10	49.5	
20 mg	5	10	5.2	
20 mg	5	10	5.3	

Three ml of freshly prepared 10% solution of potassium butylxanthogenate and 10 ml of concentrated hydrochloric acid are added to the solution in the separating funnel. The raspberry molybdenum-xanthogenate complex is extracted with chloroform (5 extracts with 10 ml portions of chloroform).

The molybdenum free solution is transferred into a 50 ml colorimeter cylinder and 10 ml of 5% sodium fluoride solution added. After several minutes, 3 ml of ammonium thiocyanate (20% solution), 2 ml of stannous chloride (35% solution in HCl), and 5 ml of isoamyl alcohol saturated with a mixture of the reagents used, are added in succession. The yellow color formed when rhenium is present is compared visually or on a colorimeter with the color of standard solutions prepared at 0.2 μg intervals over the concentration range up to 10 μg rhenium in 5 ml of isoamyl alcohol, and at 1 μg intervals over the rhenium concentration range 10 to 50 μg Re in 10 ml of isoamyl alcohol.

The accuracy of the method is ≠15%.

SUMMARY

A photometric method is suggested for the determination of small amounts of rhenium in coal, the rhenium is determined as its thiocyanate complex. Interference from vanadium is suppressed by addition of NaF. Coal samples are ashed by sintering with CaO and $KMnO_4$.

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A METHOD FOR THE DETERMINATION OF PHOSPHORUS IN PHOSPHOSILICOORGANIC COMPOUNDS

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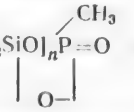
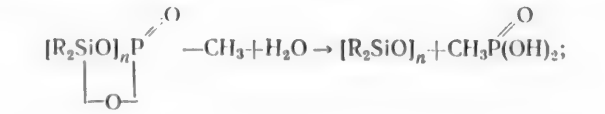
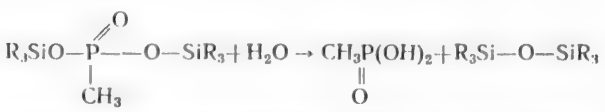
At present phosphorus is determined in phosphosilicoorganic compounds by combustion of the latter followed by separation of silicon from phosphorus. This method involves the long operation of precipitating PO_4^{3-} ions with ammonium molybdate and a titrimetric finish. In some cases, particularly during analysis of phosphosilicoorganic compounds, in which the phosphorus is connected to silicon via oxygen, simpler methods can be used. We should like to suggest that in order to determine phosphorus in phosphosilicoorganic compounds  use be made of the capacity of such compounds to be completely hydrolyzed by water with formation of alkylphosphinic acid:

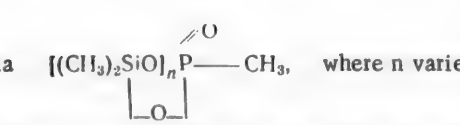




The method of determining phosphorus is very simple. 0.2-0.3 g of test material is dissolved in water and left to stand for 4-5 hr for the hydrolysis to go to completion. By heating to 80° the time necessary for complete hydrolysis can be reduced to 30-40 min. The alkylphosphinic acid liberated is titrated with 0.1 N alkali solution in the presence of thymolphthalein (pH 9.4-10.6). Results for the determination of synthetic mixtures of tetraethoxysilane and methylphosphinic acid are given in Table 1.

TABLE 1.

Taken, moles		Amt. of phosphorus, % (wt)		Difference
$CH_3PO(OH)_2$	$(C_2H_5O)_4Si$	calculated	found	
0,0067	0,018	4,76	4,98	+0,22
0,0025	0,0027	9,62	9,62	—0,00
0,0098	0,0071	12,63	12,59	—0,04
0,0098	0,0048	15,1	14,96	—0,14
0,0332	0,00825	20,9	20,73	—0,17

Compounds of the general formula  where n varied from 1 to 3 were analyzed by this method. Results which were in good agreement with the expected values were obtained in all cases (Table 2).

The agreement between parallel determinations is 0.2-0.3%

TABLE 2.

Compound	P, % found	P, % calc.	Difference	Compound	P, % found	P, % calc.	Difference
$[(CH_3)_2SiO]_3P(=O)-CH_3$ (O)	10,28	10,25	—0,03	$(CH_3)_2SiOP(=O)-CH_3$ (O)	20,34	20,18	0,16
$[(CH_3)_2SiO]_2P(=O)-CH_3$ (O)	13,64	13,29	—0,25				

SUMMARY

For determination of phosphorus in phosphosilicoorganic compounds in which phosphorus is connected to silicon via oxygen, it is recommended that use be made of the capacity of such compounds to hydrolyze with water to form alkylphosphinic acid.

AMPEROMETRIC TITRATION OF ACETYLENE IN N-METHYLPYRROLIDONE AND IN DIMETHYLFORMAMIDE WITH SILVER NITRATE SOLUTION

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Of considerable practical and theoretical interest is an examination of the possibility of using the well-known precipitation reaction of silver acetylide for the purpose of developing a direct method for the amperometric titration of C_2H_2 dissolved in N-methylpyrrolidone or in dimethylformamide.

Acetylene prepared from calcium carbide was purified with chromic mixture, cadmium acetate, and distilled water; it was then dried with silica gel and finally absorbed with N-methylpyrrolidone ($n^{25} = 1.4671$ and $d_4^{25} = 1.0321$) or diemethylformamide ($n^{25} = 1.4279$ and $d_4^{25} = 0.9470$).

The concentration of the stock solutions (about 1 M C_2H_2) was determined by weighing the solvent [1] before and after saturation with acetylene, the necessary precautions being taken to preclude loss of C_2H_2.

For polarographic determination on a dropping mercury electrode it is best to use ammoniacal solutions of $AgNO_3$ (2-10% NH_3 + 0.1 M KNO_3) in which there is linear relation between the diffusion current and the silver concentration (in aqueous solution K = 6.3 μa/mM/liter, while in aqueous methanol solution containing 50% (by volume) of CH_3OH, K = 5.5 μa/mM/liter).

The diffusion current starts at zero potential (relative to a 0.1 N calomel electrode).

All titrations were carried out on the Czech LP 55 polarograph at a potential of -0.35 to -0.40 v.

The acetylene solution was always placed in a sealed buret. Back titration of C_2H_2 with $AgNO_3$ is impossible because the C_2H_2 is expelled from the solution during removal of dissolved oxygen. Oxygen was removed by passing nitrogen through the solution for 10 min; nitrogen was passed for 1-2 min after addition of each portion of titrant.

The amperometric curves were always corrected for dilution, since the C_2H_2 concentration was only 2-20 times greater than the $AgNO_3$ concentration (Table 1).

The capillary characterisitics were as follows $mg^{2/3}\, t^{1/6} = 2.45\ mg^{2/3}\, sec^{-1/2}$ at E = 0.4 v. The cell was thermostatted at 25 ± 0.3°.

Aqueous methanol solutions (50% by volume of CH_3OH) were used for obtaining reproducible results in dimethylformamide. Under such conditions the solubility of the precipitate even increased slightly; nevertheless, the reproducibility of the results improved significantly, presumably as the result of an increase in the rate at which the acetylene is precipitated.

Characteristic amperometric curves (diagram) were obtained in all cases, the shape of these curves being influenced by the solubility of the precipitate at C_2H_2 concentrations less than 0.01 M. The reasonably large area over which the curves are linear makes it possible to determine C_2H_2 in N-methylpyrrolidone up to concentrations of 1×10^{-3} M, and in dimethylformamide up to 5×10^{-3} M (Table 1) with satisfactory accuracy.

It follows from the amperometric titration results that the following reaction occurs in ammoniacal solution:

$$C_2H_2 + Ag(NH_3)_2^+ + OH^- \rightarrow \underset{\downarrow}{C_2HAg} + 2NH_3 + H_2O. \qquad (1)$$

i.e., one mole of C_2H_2 reacts with one mole of silver.

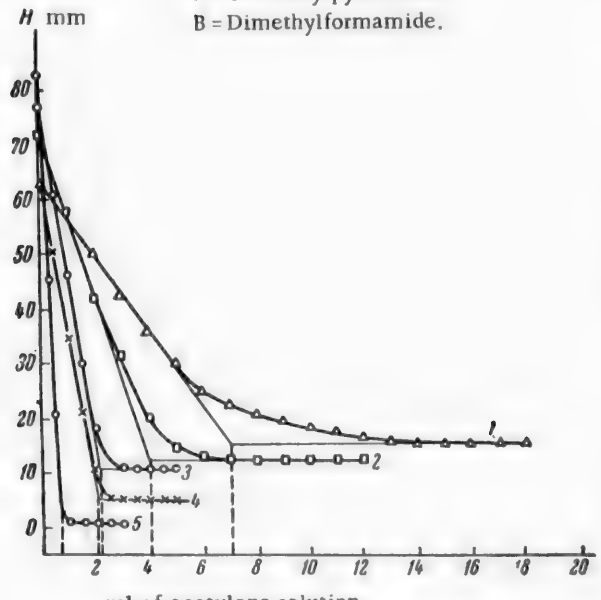
This relation was also confirmed by dissolving the precipitate in HNO_3 and determining the silver in solution.

Published information on the composition of silver acetylide is contradictory (C_2HAg, C_2Ag_2, $C_2Ag_2 \cdot AgNO_3$) [2]. Presumably the pH of the solution affects the composition of the precipitate. The most likely composition of the precipitate which separates out of acid solutions is $C_2Ag_2 \cdot AgNO_3$, while from a weakly acid (pH 4-5) buffered solution C_2Ag_2 separates out [1]. At higher pH values, as in our case, formation of C_2HAg would be expected.

TABLE 1.

C_{AgNO_3}, M	Solvent	C_2H_2 taken, M	C_2H_2 found, M	Error (relative) %
$5 \cdot 10^{-4}$	A	$1{,}02 \cdot 10^{-3}$	$1{,}07 \cdot 10^{-3}$	5,0
$5 \cdot 10^{-4}$	A	$1{,}50 \cdot 10^{-3}$	$1{,}56 \cdot 10^{-3}$	4,0
$5 \cdot 10^{-4}$	A	$2{,}01 \cdot 10^{-3}$	$1{,}97 \cdot 10^{-3}$	2,0
$5 \cdot 10^{-4}$	A	$3{,}17 \cdot 10^{-3}$	$3{,}02 \cdot 10^{-3}$	5,0
	A	$5{,}02 \cdot 10^{-3}$	$4{,}96 \cdot 10^{-3}$	1,0
$1 \cdot 10^{-3}$	B	$4{,}80 \cdot 10^{-3}$	$5{,}00 \cdot 10^{-3}$	4,0
	A	$1{,}00 \cdot 10^{-2}$	$0{,}98 \cdot 10^{-2}$	2,0
$1 \cdot 10^{-3}$	B	$0{,}96 \cdot 10^{-2}$	$0{,}95 \cdot 10^{-2}$	1,0
$2{,}0 \cdot 10^{-3}$	A	$2{,}05 \cdot 10^{-2}$	$2{,}00 \cdot 10^{-2}$	2,5
$2{,}5 \cdot 10^{-3}$	B	$2{,}40 \cdot 10^{-2}$	$2{,}38 \cdot 10^{-2}$	1,0
	A	$4{,}65 \cdot 10^{-2}$	$4{,}75 \cdot 10^{-2}$	2,0
$5{,}0 \cdot 10^{-3}$	B	$4{,}80 \cdot 10^{-2}$	$4{,}87 \cdot 10^{-2}$	1,5
$5{,}0 \cdot 10^{-3}$	A	$8{,}20 \cdot 10^{-2}$	$8{,}30 \cdot 10^{-2}$	1,2
	B	$9{,}60 \cdot 10^{-2}$	$9{,}78 \cdot 10^{-2}$	1,9
$5{,}0 \cdot 10^{-3}$	A	0,165	0,167	1,2
$1 \cdot 10^{-2}$	B	$9{,}60 \cdot 10^{-2}$	$9{,}78 \cdot 10^{-2}$	1,2
$1 \cdot 10^{-2}$	A	0,33	0,34	1,2

A = N-methylpyrrolidone.
B = Dimethylformamide.



ml of acetylene solution

Amperometric titration curves of C_2H_2 in N-methylpyrrolidone. 1 - $C_{C_2H_2} = 1 \cdot 10^{-3}$ M, $C_{AgNO_3} = 5 \cdot 10^{-4}$ M; 2 - $C_{C_2H_2} = 5 \cdot 10^{-3}$ M, $C_{AgNO_3} = 1 \cdot 10^{-3}$ M; 3 - $C_{C_2H_2} = 1 \cdot 10^{-2}$ M, $C_{AgNO_3} = 1 \cdot 10^{-3}$ M; 4 - $C_{C_2H_2} = 2 \cdot 10^{-2}$ M, $C_{AgNO_3} = 2 \cdot 10^{-3}$ M; 5 - $C_{C_2H_2} = 0.165$ M, $C_{AgNO_3} = 5 \cdot 10^{-3}$ M

The solubility of acetylides decreases with increasing pH [3]. Ammonia, should, on the one hand, depress the solubility by increasing the pH, while on the other hand, it should increase the solubility as a result of complex formation with silver. As is to be expected (equation 1), changes in NH_3 concentration over the range 2-10% do not appreciably affect the character of the amperometric curves.

Using equation 1 and the instability constant $K_C = 2.75 \times 10^{-8}$ for $Ag(NH_3)_2^+$ [4], we calculated the "product of hydrolytic solubility" constant suggested by Babko and Grebel'skaya as a characteristic of the solubility of acetylides:

$$L_h = [Ag^+]\,[C_2H_2]\,[OH^-]. \qquad (2)$$

For this purpose we initially found the value (all calculations were made for aqueous solutions):

$$L = [Ag(NH_3)_2^+]\,[C_2H_2] = \left(\frac{i_{equiv.}}{K}\right)^2, \qquad (3)$$

which for $[NH_3]$ = const and $[OH^-]$ = const is constant (Table 2) and characterize the limit of sensitivity of amperometric titration ($i_{equiv.}$ is the current strength at the equivalence point, and K is the diffusion current constant).

The value L = 3.8×10^{-8} (for $[NH_3] = 6.1$ and $[OH^-] = 1.0 \times 10^{-2}$M) shows [5] that the sensitivity of the technique should not be less than 10^{-3} - 10^{-2} M C_2H_2, this was actually observed experimentally.

TABLE 2.

C_{AgNO_3}, M	$C_{C_2H_2}$, M	Iequiv, μa	$L_h \cdot 10^8$
$5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	0,705	(1,3)
$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	1,27	4,1
$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	1,16	3,4
$2 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	1,24	3,9
$5 \cdot 10^{-3}$	0,165	1,25	3,9
		Mean	3,8

The value $L_h = 10^{-19}$. It was found in [3] that

$$L_h = [Ag^+]^2 [C_2H_2] [OH^-]^2 \cong 10^{-37}, \quad (4)$$

since it was assumed [3] that C_2Ag_2 is precipitated from ammoniacal solution. If the results on the solubility are used [3] and it is assumed, as we have established, that the composition of the precipitate is C_2HAg, the value obtained for L_h is about 10^{-20}. Bearing in mind that the solubility was studied [3] in very acid solutions, while our results were obtained in strongly ammoniacal solutions (the difference in $[OH^-]$ is more than ten times greater), the value of $L_h = 10^{-19}$ - 10^{-20} can be regarded as a fully reliable value for the precipitate of C_2HAg.

SUMMARY

A precipitation reaction of silver acetylide in which the diffusion current of silver ammonite ions is recorded, has been used for the amperometric titration of acetylene solutions (in a buret). The sensitivity of the reaction is 1×10^{-3}M of acetylene. The experimental accuracy is 1-2% (relative) for acetylene concentrations in excess of 5×10^{-3}M.

It has been established that the composition of the silver acetylide precipitated from ammoniacal solution corresponds to the formula $AgHC_2$; the hydrolytic solubility product of this precipitate has been found to be $L_h = 10^{-19}$ - 10^{-20}.

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DETERMINATION OF PHOSGENE IN THE PRESENCE OF CHLORINE AND HYDROGEN CHLORIDE

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We encountered considerable difficulties during determination of phosgene in the presence of chlorine and hydrogen chloride. A number of methods have been described; an iodometric method [1], and an aniline [2] method based on absorption of phosgene with an alcoholic solution of alkali, or with an ammoniacal solution of silver nitrate [3], with subsequent determination of halide gravimetrically or titrimetrically. All these methods only permit determination of phosgene in the absence of chlorine, hydrogen chloride, and other impurities. Antimony metal, antimony sulfide, mercury, and mercuric sulfide have been suggested for absorbing chlorine, while zinc dust has been suggested for absorbing hydrogen chloride. This complicates an analysis considerably.

We should like to suggest a new method for determining phosgene, which is based on the interaction of phosgene with hexamethyleneimine [4], with subsequent titration of excess of the latter after steam distilling it from an alkaline solution. Bis-hexamethyleneurea which is formed according to the equation:

$$4(CH_2)_6NH + COCl_2 \rightarrow (CH_2)_6N—CO—N(CH_2)_6 + 2(CH_2)_6NH \cdot HCl,$$

does not hydrolyze under the experimental conditions used.

Phosgene was prepared from carbon tetrachloride and oleum, it was purified by freezing it twice and was finally dissolved in toluene. Dioxane or toluene was used as solvent for hexamethyleneimine; toluene is less suitable because of its insolubility in water which complicates distillation and titration. Poor results were obtained with aqueous solutions of hexamethyleneimine, as might have been expected, because of the hydrolysis of phosgene with water.

The distillation apparatus consists of an ordinary Wurtz flask with an outlet tube bent through a right angle, a pipet being fused to it. The tip of the pipet was immersed in a measured volume of 0.1 N acid.

Results for the determination of pure phosgene are given in Table 1. As a control, the chloride content of the solution remaining in the flask after the hexamethyleneimine had been steam distilled off was determined by the Volhard method.

The method permits phosgene to be determined in the presence of chlorine and hydrogen chloride. The latter is bound by the hexamethyleneimine into a salt, while the chlorine forms a chloramine which can be destroyed by addition of sodium sulfite. All the hexamethyleneimine which has not been used up in forming the urea derivative is distilled off from the alkali solution.

An aliquot of phosgene in toluene, taken in an ampoule, was dissolved in dioxane in a standard flask. Phosgene was determined in one aliquot as described below. A solution of chlorine in carbon tetrachloride was added to another aliquot and the phosgene determined again. The amount of phosgene found in the pure sample and in the presence of chlorine coincides (Table 2).

Experimental Method. Pure Phosgene and Phosgene in the Presence of Hydrogen Chloride. An aliquot of a solution of phosgene in toluene (0.05-0.1 g), taken in an ampoule, is introduced into a flask with a ground stopper and 5 ml of a solution of hexamethyleneimine* in toluene or dioxane** (5 g of hexamethyleneimine in 100 ml solution),

* The hexamethyleneimine is dried with solid potassium hydroxide and distilled, b.p. 138°.

** Dioxane is purified by distillation over sodium.

added from a pipet. The flask is stoppered and vigorously shaken; as a result the ampoule containing the phosgene is broken and the flask is allowed to stand for several minutes for the mist to settle. The contents of the flask are transferred to the distillation apparatus, it is rinsed with 30 ml of water, and 5 ml of 40% alkali solution added. Distillation is then carried out into 50 ml of 0.1 N acid. Excess acid is determined by titration with 0.1 N alkali using a mixed indicator of methyl red – methylene blue (40 ml of a 0.1% alcoholic solution of methyl red is mixed with 10 ml of a 0.1% alcoholic solution of methylene blue and 50 ml of alcohol and 100 ml of water added). The end point is established by a sharp change from rose to green. A blank is carried out in the same way (using the same amounts of reagents and carrying out the distillation) except that an aliquot of phosgene is not taken.

TABLE 1.

Wt. of $COCl_2$, taken, g	V***	$COCl_2$ found, %	
		on the basis of chlorine	on the basis of hexamethyleneimine
0,1011*	3,97	19,44	19,39
0,1047*	4,09	19,18	19,91
0,0403*	1,62	19,85	19,90
0,0734*	2,95	19,91	19,89
0,1280**	4,90	19,01	19,26
0,0633**	2,35	18,41	18,45
0,0992**	3,82	19,06	18,66

* Hexamethyleneimine in dioxane solution.

** Hexamethyleneimine in toluene solution.

TABLE 2.
(0.04836 g phosgene in toluene taken)

$COCl_2$, pure, %	$COCl_2$ in the presence of chlorine, %
15.97	16.32
15.77	16.21
16.21	15.97
16.20	15.77
Mean 16.04%	16.07%

The formula used for calculation is:

$$\%COCl_2 \frac{(v_1 - v_2) \cdot N \cdot M \cdot 100}{a \cdot 2 \cdot 1000},$$

where v_1 is the amount in ml of alkali used for titrating the aliquot of phosgene; v_2 is the amount in ml of alkali used for titrating the blank; N is the normality of the alkali; M is the molecular weight of phosgene; a is the weight of the aliquot (in g).

Phosgene in the Presence of Chlorine. When the phosgene contains chlorine as an impurity, 5 ml of 0.5 N sodium sulfite solution (120 g of the heptahydrate in one liter of water) is added to the solution when the reaction between hexamethyleneimine and phosgene is complete; the determination is then finished as described above.

SUMMARY

A new method has been developed for the determination of phosgene which is based on the reaction of the latter with hexamethyleneimine, with subsequent determination of excess of the imine. The method permits determination of phosgene in the presence of chloride and hydrogen chloride.

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CRITICISM AND BIBLIOGRAPHY

A. I. BUSEV. THE USE OF DIVALENT CHROMIUM COMPOUNDS IN ANALYTICAL CHEMISTRY

Moscow. Viniti AN SSSR, 1960, 164 pp. Bibl. 180 refs.
Reviewed by P. P. Shat'ko
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 745-746, November-December, 1961

Divalent chromium ions have a number of advantages as a reducing agent over other reducing agents (vanadyl sulfate, trivalent titanium salts, potassium stannite, sodium hydrosulfite, hypophosphorous acid etc.). The most important advantage of divalent chromium is its strong reducing capacity. The ease of preparation and storage of stable solutions of divalent chromium salts ensures the further introduction of chromometry into practical work as the author correctly points out. A. I. Busev's monograph is of undoubtedly great interest for a wide circle of analytical chemists as the first complete summary of accumulated experience in the application of divalent chromium compounds in analytical chemistry.

The first section of the book is devoted to general questions of the application of divalent chromium compounds in analytical chemistry. Methods of preparing, standardizing, and storing standard solutions of divalent chromium salts are described in detail.

The second section is devoted to the reduction reactions of elements with divalent chromium compounds and the use of such reactions in analytical chemistry. The heading of the second section does not correspond in all respects to its contents, since the author in this section gives a detailed review of methods for the quantitative determination and separation of the ions of different elements which are reduced by divalent chromium ions. Reduction of the following elements is considered: of group I elements Cu^{2+}, Ag^{+}, Au^{III} (pp. 28-39); of group II, Hg^{2+}, Cd^{2+} (pp. 39-41); of group III, Ce^{IV} (pp. 41-42); of group IV, Sn^{IV}, Ti^{IV} and carbon compounds (pp. 42-60); of group V, N^{V}, As^{V}, Sb^{V}, Bi^{III}, V^{V} (pp. 60-78); of group IV, O_2, S^{VI}, Se^{IV}, Te^{IV}, Cr^{VI}, Mo^{VI}, W^{VI}, U^{VI} (pp. 78-117); of group VI, Br_2, I_2^-, I^{V}, Br^{V}, Mn^{VII} (pp. 117-121); and of group VII, Fe^{3+}, Co^{III}, Ru^{III}, Os^{IV}, Rh^{III}, Jr^{IV}, Pe^{IV} (pp. 121-155). The methods indicated for the determination of each element in pure solutions, in mixtures, and in various samples are of practical importance (ores, special steels, etc.). The review of the reduction of organic compounds is of considerable importance, and this should be reflected in the heading.

A factor which complicates reading of the monograph is the absence of the names of the authors during a description of most of the methods of determination, only the ordinal number being given in the literature reference, and this sometimes leads to errors; thus on p. 72 (13 lines from the bottom) [122] is written whereas it should obviously be [123]. There are other small errors. On p. 10 (one line from the top) the author states that the "reducing properties of divalent chromium increase with decreasing acid concentration." We cannot agree with such an unconditional generalization, since it is known that the reducing properties of Cr^{2+} with respect to arsenates increase, rather than decrease, with increasing acid concentration. In dealing with the reduction of dichromate to a trivalent chromium salt by means of ethanol, concentrated hydrochloric acid, or hydrogen peroxide (p. 12), the author does not point out that such a reduction can be effected by means of ethanol and concentrated sulfuric acid.

Unfortunately, the methods of preparing solutions of divalent chromium salts are not given in chronological order. Thus the work of Stone and Bison (1936) is mentioned before that of Thornton and Sadex (132). Stone and Bison modified Thornton and Sadex's method. The author does not refer to Popov's method of preparing divalent chromium salts (Zavodsk. laboratoriya 12, 972 (1946)). We do not think it is a good idea to standardize the Cr^{2+} solution against ferric iron (p. 20) on the grounds that it necessitates a parallel titration of two solutions. The Cr^{2+} solution is best standardized against cupric sulfate, whose titer is established electrolytically. The method of microtitration in ultraviolet light should not be described on p. 28, since it does not belong to this chapter.

On p. 28 the author notes that Cu^{2+} ions are reduced immediately in a sulfuric acid medium to the elemental state, while on p. 34 it is stated that during titration of a hot sulfuric acid solution of cupric sulfate with $CrSO_4$, no deposition of metallic copper is observed right at the beginning, but cuprous sulfate is formed which subsequently

disproportionates to metallic copper and $CuSO_4$. On p. 35 (23 lines from the top) while dealing with paper [95] published in 1943, the author mentions a similar paper on the determination of copper [71] published in 1938 only mentioned on 63. We do not agree that CO_2 removes Cl_2 (a heavier gas) from solution without boiling the solution (p. 71). Of interest to the reader is a technique for the determination of oxygen dissolved in water in the presence of nitrites, consequently it should be mentioned on p. 79. On p. 83 the author points out that during titration of a solution containing Se^{4+} and Cu^{2+} in a medium of 9 N HCl at 70°, in a medium of 6 N HCl at room temperature, and in a medium of 6 N H_2SO_4 at 70°, with a solution of chromous sulfate, selenium is always reduced first. On p. 84 it is stated, however, that "in a medium of 6 N H_2SO_4 at 70° there is observed simultaneous reduction of copper with quadrivalent selenium." This contradiction should be removed. There is an unfortunate expression on p. 88 (20 lines from the bottom) "a distinct potential jump of the platinum electrode was observed on completion of its reduction to the quinquevalent state." The theoretical bases of the standardization of solutions of divalent chromium salts by Stone's method are not described clearly enough.

There are many minor mistakes in the book.

All the shortcomings noted do not detract from the general good impression created by the monograph reviewed, which is undoubtedly necessary and useful. The monograph will be welcomed with great interest by its readers.

ALEKSANDR PETROVICH TERENT'EV

(On his 70th Birthday)

Commission on Analytical Chemistry
Editorial Board of Zhurnal Analiticheskoi Khimii
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 747-748, November-December, 1961

Aleksandr Petrovich Terent'ev, one of the most outstanding Soviet organic chemists, a corresponding member of the Academy of Sciences, USSR, and a professor of Moscow University celebrated his seventieth birthday in 1961. A student and coworker of N. D. Zelinskii, he has taken over in full the broad scientific interests and the original teaching mastery of his teacher. A. P. Terent'ev has developed and introduced into practice a number of new synthetic methods which have found use for various classes of organic compounds.

An important feature of A. P. Terent'ev's work is the synthesis and study of the properties of organic complex compounds, and, in particular, intracomplex compounds. He has made a particularly important contribution to organic analysis.

A characteristic feature of A. P. Terent'ev's scientific achievements is his endeavour to extend the field of application of the new reactions and compounds he has studied. In this connection no less important is their use in analysis. Thus having done a considerable amount of work on the synthesis of diazo compounds, A. P. Terent'ev suggested a method for the quantitative determination of compounds with conjugated short bonds by coupling with diazotized p-nitroaniline (1936). This method possesses a high sensitivity and permits determination of conjugated dienes in the presence of a large excess of olefins.

By studying the structure and properties of magnesium organic compounds, A. P. Terent'ev basically improved the Chugaev-Zerewitinov method of determining active hydrogen. The Zerewitinov method involves a difficult measurement of the volume of methane liberated on the basis of the expansion of the gas, and in this connection it is envisaged that the reaction is carried out, not in ether, but in a high boiling solvent.

A. P. Terent'ev (1940-1947) when using the Chugaev method for the determination of active hydrogen, adopted the technique of expelling the methane liberated with ether vapor, which essentially simplified the apparatus and experimental technique, and enabled a more active ethereal solution of the magnesium organic compound to be used which cut down the time of a determination several times. Determination of active hydrogen by the Chugaev-Terent'ev method is widely used both in scientific research and for production control.

A. P. Terent'ev has suggested an original method for the analysis of oleum which is widely used in many laboratories.

In the first post-war years A. P. Terent'ev together with coworkers finished developing methods for the sulfonation of organic compounds with sulfur trioxide bound as a complex. They used this powerful synthetic method for analytical purposes for the quantitative determination of certain forms of active hydrogen. For example, by the action of a standard solution of sulfur trioxide on a hydroxyl compound an alkylsulfuric acid is formed which is then diluted with water and titrated with alkali. From the titer difference it is possible to assess the amount of sulfur trioxide which has reacted, i.e., to assess the equivalent of the hydroxyl compound. The method is distinguished by the fact that appreciable amounts of water do not interfere. Many other forms of active hydrogen and certain functional groups have been determined in a similar way.

Toward the end of the thirties A. P. Terent'ev devoted a lot of time to a study of the properties and reactions of acrylonitrile. On the basis of this work A. P. Terent'ev et al. developed a number of methods for the quantitative determination of acrylonitrile. The most interesting and effective method is the quantitative interaction of acrylonitrile with sodium sulfite in aqueous solution. During this reaction sodium hydroxide is liberated which can be titrated by any known method. Having acquired such a convenient method of determining acrylonitrile, A. P. Terent'ev with his characteristic perspicacity, has already used it for the analysis of a number of cyanoethylated

compounds. An aliquot of the compound is mixed with a standard solution of acrylonitrile and the unreacted acrylonitrile backtitrated after a definite time. This method has proved exceptionally convenient for the determination of thioalcohols, thiophenols, etc.

The brilliant imagination and exceptional inventiveness of A. P. Terent'ev has enriched many branches of chemical organic analysis. In the field of elemental organic analysis, he and his student, now Doctor of Science, P. N. Fedoseev have suggested methods of decomposing organic compounds with magnesium, calcium, and magnesium nitride.

In another series of papers A. P. Terent'ev and B. M. Luskina developed a new, practically valuable variant of the "wet combustion" technique which permits simultaneous determination of carbon, halogen, and nitrogen, and also metal ions and silicon in the mineralized residue.

In the field of inorganic analysis A. P. Terent'ev et al. have suggested a number of new organic reagents. A. P. Terent'ev's idea of "in situ nascendi reagents" which has been developed by a number of authors is interesting and fruitful. The ions to be precipitated and the precipitant ions are present in solution, not in a ready state, but in a bound form, the inorganic ions, in the form of unstable complex compounds, the precipitant, in the form of organic compounds. The latter on hydrolyzing liberate the necessary ions in the solution. Slow formation of precipitant and the ion to be precipitated promotes the formation of well formed crystals. For example, A. P. Terent'ev suggested the use of dimethyl sulfate in the presence of sugar for the precipitation of barium ions. Under such conditions exceptionally large and readily filtrable crystals of barium sulfate are formed. Under the same conditions, but in the presence of dioxane, calcium is precipitated as $CaSO_4 \cdot 0.5H_2O$, and in this way can be determined in the presence of appreciable amounts of strontium.

A large monograph would be necessary to catalogue the numerous and diverse researches of A. P. Terent'ev in the field of analytical chemistry, but the significance of A. P. Terent'ev's activity for Russian organic analysis could not be exhausted by any method.

A. P. Terent'ev is rightly regarded as an outstanding organic analyst. This is not simply because he has created a school of analysts, and that hundreds of his pupils are working successfully in various corners of our country. A. P. Terent'ev is an untiring propagandist of new, progressive methods of analysis, a severe critic, and an invaluable and kind consultant. On his recommendation, and under his editorship, a series of valuable analytical textbooks have been published in Russian: A. P. Terent'ev has been for many years an active member of the Commission on Analytical Chemistry and a member of the editorial board of "Zhurnal Analiticheskoi Khimii."

We should like to wish him new, important, creative successes in all his manifold scientific, social, and teaching activities.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) } Dokl(ady) AN SSSR }	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences: Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Life Sciences: Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Life Sciences: Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences: Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Mathematics: Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics: Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Physics: Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1961
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. met.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals		6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica		1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PTÉ	(see Pribory i tekhn. éks.)					
	Problemy Severa	Problems of the North	National Research Council of Canada			
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
	Stal'	Stal (In English)	Iron and Steel Institute		1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1960
Usp. fiz. nauk	(see UFN)					
Usp. khim(ii)	(see UKh)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958

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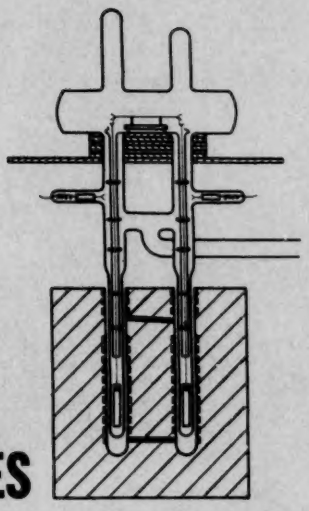

VOLUME I

VACUUM MICROBALANCE TECHNIQUES

Proceedings of the 1960 Conference Sponsored by
The Institute for Exploratory Research
U. S. Army Signal Research and Development Laboratory

Edited by
M. J. KATZ
U. S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Introduction by
Thor N. Rhodin
Cornell University

The proceedings of this conference provide an authoritative introduction to the rapidly widening scope of microbalance methods which is not available elsewhere in a single publication.

The usefulness of microbalance techniques in the study of the properties of materials lies in their extreme sensitivity and versatility. This renders them particularly important in studies of properties of condensed systems. In addition to the historical use of microbalance techniques as a tool of microchemistry, they have, in recent years, found extensive application in the fields of metallurgy, physics, and chemistry. The uniqueness of the method results from the facility it provides in making a series of precise measurements of high sensitivity under carefully controlled conditions over a wide range of temperature and pressure.

This significant new volume contains papers in three major categories. The first group of reports deals with the general structural features and measuring capabilities of microbalances. In the second group, a sophisticated consideration and much needed evaluation of sources of spurious mass changes associated with microbalances is presented. The third group describes some of the most recent extensions in microbalance work to new research areas such as semiconductors, ultra-high vacuum, and high temperatures. These papers provide an interesting account of advances in the application of the microgravimetric method to three new and important fields of research on the behavior of materials.

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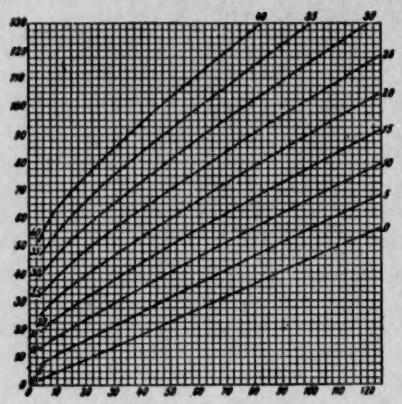

TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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II. Table for converting milligram-equivalents of Ca^{2+}, Mg^{2+} and HCO_3^- into German degrees of hardness

III. Tables for converting milligrams into milligram-equivalents

IV. Tables for converting milligram-equivalents into milligrams

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Factors for converting the results of water analysis from one form into another

Average value of activity coefficient f_{av}

Nomogram for calculating percent-equivalents

Nomogram for calculating p[illegible] from given values of free CO_2 and HCO_3^-

Calculation of aggressive carbon dioxide

Relation between different forms of weak acids in natural waters at different pH values and ionic strengths μ

Factors for converting different forms of expressing aqueous solution concentrations into milligrams and milligram-equivalents

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